

NATIONAL GROUND WATER ASSOCIATION

Presents

**The Southwest Focused Ground Water Conference:
Discussing the Issue of MTBE and Perchlorate in
Ground Water
Supplement**

Co-sponsors:

**American Petroleum Institute
California Groundwater Association
Association of California Water Agencies
Groundwater Resource Association of California
Western States Petroleum Association**

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Keynote speech for Walt Pettit
“California Water: Is It Safe?”
National Groundwater Association Conference
June 3, 1998
Anaheim, California

Methyl Tertiary Butyl Ether (MTBE)
and Perchlorate in Groundwater

- Thank you -- It's my pleasure to introduce the topics for the next two days of discussion. The agenda for the two constituents under discussion looks great.
- However, I can't help contrasting the assigned title for my presentation (California Water: Is it Safe?) with the scope of the agenda.
- I think the short answer to the question is pretty much “yes”. At least I don't hesitate to drink public water supplies anywhere in the State, and I sample a number of them. That doesn't mean we are lacking problems. A lot of expensive fixes and protection efforts are going to be a part of our everyday business for the foreseeable future. Limited supplies in some areas and an expanding population will exacerbate the problem.
- However, my point is this: The answer to the question “Is it Safe?” involves a lot more than MTBE and Perchlorate, particularly in the long run. For example, how much threat is posed by nitrate trends in the San Joaquin and Salinas Valleys? Will San Diego's Repurification project prove out? For that matter, will it survive the opposition so it can be tried? How serious is the bromide problem in Bay-Delta water supplies? Will dioxin be a universal problem as a result of air deposition?

- As a matter of personal perspective, I believe those issues have the potential to drive Statewide water policy in coming years to a greater extent than our immediate subjects.
- That said with respect to perspective, I don't want to minimize the need to deal with MTBE and Perchlorate, and the agenda for this conference looks very promising.
- Let's turn now to MTBE.

MTBE

- In addition to episodic problems, State and local agencies have been cleaning up petroleum products, solvents, and rocket fuels for years, along with the usual sewage spills, fish kills, and railroad accidents. It should be obvious that my Board doesn't want any of that stuff in the water and we go to great lengths to keep it out. I wouldn't be surprised if representatives of some of the sponsoring organizations have complained to Legislators and others that some of our efforts in that regard have been excessive. We have been criticized from both directions with respect to our response to MTBE pollution.
- Having been grilled by legislative committees, water quality experts, water suppliers, leaking tank owners, consultants, equipment suppliers, environmental groups, etc., I think I'm in a position to confirm that MTBE is a very contentious subject.
- In April, the Sierra Club, the Planning and Conservation League and the American Methanol Institute issued a report questioning whether the State is protecting drinking water from gasoline contamination, with an emphasis on MTBE. We prepared a response based upon our opinion that the report was something less than the "good science" which is everyone's buzz phrase these days.

- However, to no one's surprise, in response to this report, the Joint Legislative Audit Committee ordered an audit of the State Water Resources Control Board (SWRCB), the Department of Health Services (DHS), and the Office of the State Fire Marshall. That is just an indication of the emotional impact of MTBE. We don't object to audits. If anyone wants to look at our operations, they are always welcome and entitled to do so. However, in this case, it appears that the timing could have been better synchronized with all of the ongoing work, which I am going to summarize.
- The threat that MTBE poses to California's water resources is a grave concern to us and to water suppliers in particular. The State Administration is taking immediate and thorough action to examine all aspects of MTBE.
- MTBE is found in shallow groundwater beneath many leaking tank sites. The implication that deeper groundwaters, which typically supply drinking water, have been widely affected, or are at great risk, is not generally evident in sampling results of those waters. Santa Monica is one of the exceptions. You will hear more about the specifics of exceptions as the conference progresses.
- We have seen no evidence to support the contention that there is widespread leakage from properly installed upgraded underground tanks. The upgrade program (all tanks installed prior to 1984 must be upgraded or replaced by December 22, 1998) will not guarantee there will be no leaks. However, leaks should be the exception and when they occur they will be responded to as is any other unintended discharge. Improved monitoring will greatly enhance the early-warning system.
- As a result of several pieces of legislation and a Governor's Executive Order issued last year, a number of State agencies are now working to determine the future of MTBE in California (*SWRCB, 9 Regional Boards, DHS, Energy Commission, Office of Environmental Health Hazard Assessment (OEHHA), Department of Water Resources, and the University of California*). That doesn't include the ongoing work of the oil industry, the water suppliers, and others.

- In October 1997, the Governor signed into law legislation designed to answer a number of outstanding questions about MTBE, and to provide the best information available while the answers are being developed.

The on-going efforts include the following:

- The Local Drinking Water Protection Act was adopted. It contains many components, principal among which is developing a secondary water standard (taste and odor) by July 1, 1998, and a primary standard (health-based) by July 1, 1999. The DHS has publicly proposed a 5 parts per billion (ppb) taste and odor standard for public consideration and adoption. OEHHA held a hearing May 15 on their proposed public health goal for MTBE of 14 ppb. If this goal is adopted by OEHHA, it will then be submitted to DHS for consideration as a primary standard.
- By January 1, 1999, the California Drinking Water and Toxic Enforcement Act Scientific Advisory Panel must recommend to the OEHHA whether or not MTBE should be listed as a carcinogenic toxin.
- Each Regional Water Quality Control Board must publish and distribute, on a quarterly basis to all public water system operators within each region, a list of MTBE discharges occurring during the previous quarter, together with a list of locations where MTBE was detected in groundwater.
- With evidence showing that MTBE appears in groundwater primarily as a result of leaking underground storage tanks, new law requires the SWRCB to establish a data system to track these tanks and their discharges.
- \$5 million will be appropriated annually to reimburse public water systems for treatment or alternative water supply costs should MTBE pollute a water source.
- The newly-created MTBE Public Health and Environmental Protection Act has given the University of California \$500,000 for an assessment of health effects data for MTBE and other oxygenates, and the risks

associated with their use. This report, to be completed by January 1, 1999, requires the Governor, based on the UC report and comments from two public hearings, to certify whether MTBE poses a risk to human health or the environment. He is required to take action, if warranted, to protect public health and the environment.

- To reduce the possibility of leaks from underground tanks and associated piping, Governor Wilson signed into law legislation we sponsored, effective January 1, 1999, prohibiting distributors from supplying gasoline to operators of tanks not upgraded or replaced prior to the December 22, 1998 federal and State deadline.
- Completion of the tasks required by legislation is needed to develop an intelligent statewide response to the threats MTBE poses.
- In addition to these new laws, the Governor directed the SWRCB to convene an UST Advisory Panel comprised of over 30 representatives of industry, government and water agencies to:
 1. Evaluate the effectiveness of the new UST systems required by the end of this year (their report is due October 1); and
 2. Evaluate marina refueling practices (their report is due July 1).
- In addition, a new report prepared at our request by the Lawrence Livermore National Laboratory addressing MTBE in groundwater is due for release late this week or early next week. This will be an interim report. Lawrence Livermore has found information on a number of sites that had monitored MTBE for several years, so additional time has been requested to analyze this data. The interim report, however, will contain many findings and valuable information. The final report is due by September 30.
- As these studies and panels proceed, the DHS continues to require all public water suppliers to monitor their drinking water sources, both wells and surface waters, for MTBE. Through 1997, 23 percent, or 2,553 of the 11,000 drinking-water sources, have been sampled for MTBE. Of those sampled, 1.3 percent or 33 sources, had detectable

MTBE levels. Of those 33 sources, approximately 1/3 had levels above the State's interim drinking water "action level" of 35 ppb.

- I have concentrated on public supplies, but we can't ignore the fact that some private water suppliers have been substantially impacted. Just last night, a colleague told me of an MTBE hit in a very small system in Sacramento, at a concentration of 20 ppb. Finds at levels right around the likely future primary standard will be particularly difficult to deal with in the interim period between now and the time a standard is adopted.
- As the sampling data base expands, while MTBE continues to migrate, the recorded number of impacted supplies will increase. In other words, the physical situation may not change, but our increased knowledge of it indicates that matters will continue to get worse before they get better.
- Because MTBE is now being detected in minimal amounts in many of the State's domestic use reservoirs and natural lakes, attention is turning to the likely cause - boat exhaust, primarily from two-stroke marine engines and fuel spillage. High MTBE readings have been reported at docking areas and not from areas where public drinking water is taken. Water districts have the power to curtail or halt any type of activity with the potential to reduce the quality of their domestic water supply but efforts to limit use of two-stroke engines have been as controversial as other aspects of MTBE.
- To maintain Lake Tahoe's pristine integrity, the Governor has included \$150,000 in his 1998-99 budget for vital monitoring activities.
- Finally, in the event that the use of MTBE will be reduced or eliminated, the Legislature has directed the California Energy Commission to study the potential impact such action would have on California's gasoline supply.
- It is interesting to note that Tosco Refining Company in April began substituting ethanol for MTBE in 3 San Francisco Bay area counties as part of a six month pilot program to explore alternatives to MTBE.

- Tosco has been quoted as saying it hopes the program “will encourage state and federal legislators to give oil companies more flexibility in reformulating gasoline to reduce pollution.” (*reference to Feinstein Bilbray legislation*)
- MTBE poses a vexing problem. While its positive effects at restoring our air quality have been well documented, it is just one of many chemicals that we don’t want in our drinking water at any level.
- Governor Wilson has called into action California’s wide array of scientists, technicians, and regulators. Their results will guide the State in determining the future of MTBE in California.

Perchlorate

- Perchlorate has been used in manufacturing solid rocket propellants, munitions and fireworks. Sources of drinking water have been contaminated by Perchlorate in areas in which such manufacturing or rocket testing occurred.
- Pollution has been found at 6 Superfund sites in California (Aerojet, Mather AFB, San Gabriel Valley, NASA-JPL, Edwards AFB, and San Fernando Valley); as well as 6 non-Superfund sites in California, and a Nevada site that could affect Nevada, Arizona, and California.
- Currently, there is limited toxicity data available. The contaminant is not regulated by the Safe Drinking Water Act.
- Because Perchlorate historically has not been considered a common drinking water contaminant, no federal or State drinking water standards exist and there is no standard treatment technology at this time. However, a large treatment facility to remove Perchlorate from extracted groundwater is being constructed at Aerojet. It will be operational by the end of August 1998. This treatment method is not for water supply wells. It is a groundwater extraction treatment system for containment of a plume. The water from the system won’t be directly used by the

consumer. This treatment method will eliminate the injection into the aquifer of Perchlorate above 18 ppb, the action level specified by DHS.

- Efforts to obtain additional toxicological data are underway. The Air Force and an industry group are conducting a series of animal toxicological studies. EPA has reviewed and commented on that work. A revised provisional reference dose is expected by September 1998. EPA will sponsor a review of this analysis by an external scientific panel to be completed in October 1998.
- A bill is pending in the Legislature to mandate that DHS adopt a State primary drinking water standard for Perchlorate by July 1999.

In summary, the problem posed by these two constituents is substantial, and the news may get worse before we turn the corner and get it under control. However, the horsepower mobilized to deal with the issue, much of which is represented here, is immense. In the meantime I suspect that drinking from public water supplies is one of the less risky things we do.

OXYGENATE USE IN GASOLINE--WHEN, WHAT, AND WHY

L. M. Gibbs
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Ethanol dates back to antiquity while tertiary alkyl ethers were first produced in 1907. Ethanol was first blended with gasoline in the U.S. in the 1930s and 1940s. However, broad usage of ethanol didn't occur until after 1978. It was used then to increase octane quality and to extend the gasoline supply. Other alcohols, such as tertiary-butyl alcohol, have been used as early as 1969 and were blended with methanol in 1981. As a result of regulatory changes, methanol blends are no longer being used.

The tertiary alkyl ether, methyl *tertiary*-butyl ether (MTBE), came on the commercial gasoline scene in 1979. It was first used to increase octane quality and to help comply with federal lead phasedown requirements. Other ethers, such as *tertiary*-amyl methyl ether (TAME), ethyl *tertiary*-butyl ether (ETBE), and diisobutyl ether (DIPE) also have been used. MTBE currently is the most widely used oxygenate, especially in reformulated gasoline, which is required for severe ozone nonattainment areas. These are areas that do not meet federal ozone ambient air quality standards. Both MTBE and ethanol are used in wintertime oxygenated gasoline in areas not meeting carbon monoxide ambient air quality standards.

The following charts present information on what oxygenates are being used, how they are made, why they have been used in the past, and why they are being used now. A detailed history of their evaluation and use and a summary of the regulations that control their use are provided. The presentation includes two tables that provide physical and chemical properties for five alcohols and six ethers that are or can be blended with gasoline. Various properties are compared as a function of the number of carbon atoms in the various alcohols and ethers. Finally, there are charts providing information on why certain oxygenates are used in reformulated gasoline and in oxygenated gasoline.

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Oxygenate Use in Gasoline When, What, and Why

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**National Ground Water Association Conference
June 3-4, 1998**

What is an Oxygenate?

According to ASTM:

**An oxygen-containing, ashless, organic compound,
such as an alcohol or ether, which can be used
as a fuel or fuel supplement.**

What Oxygenates Are Being Used?

- Methyl *Tertiary-Butyl* Ether (MTBE)
- Ethanol
- *Tertiary-Amyl* Methyl Ether (TAME)
- Diisopropyl Ether (DIPE)
- Ethyl *Tertiary-Butyl* Ether (ETBE)
- *Tertiary-Butyl* Alcohol (TBA)

How Are They Made?

- ♦ Ethanol -- C_2H_5OH
Fermentation (Primarily of Corn)
- ♦ MTBE -- $(CH_3)_3COCH_3$
Catalytic Reaction of Isobutylene, $(CH_3)_2C=CH_2$,
and Methanol, CH_3OH

Why Are They Used?

- **Late 1970s and 1980s**
 - **Octane Enhancer**
 - **Meet Lead Phasedown Requirements**
 - **Fuel Extender**
- **Now**
 - **Meet Reformulated Gasoline Requirements**
 - **Meet Wintertime Oxygenated Gasoline Requirements**
 - **Octane Enhancer**
 - **Fuel Extender**

When Studied, Used, or Regulated

- **1907-- First Tertiary Alkyl Ether (TAME) Produced**
- **1930 -- Agrol (Ethanol Blend) Marketed in Nebraska**
- **1934 -- First Tertiary Alkyl Ether Synthesis U.S. Patent Issued**
- **1940 -- Alky-Gas (Ethanol Blend) Marketed in Nebraska**
- **1968 -- Chevron Taxicab Field Test of MTBE/TAME**
- **1969 -- ARCO Blended Tertiary-Butyl Alcohol**
- **1977 -- Clean Air Act Amendments Requiring Waivers**
- **1978 -- Nebraska Gasohol (Ethanol Blend) Program Begins**
- **1978 -- EPA Waiver Issued for 10 vol % Ethanol**
- **1979 -- EPA Waiver Issued for 7 vol % MTBE -- Use Begins**

When Continued

- 1979 -- EPA Waiver Issued for 2.5 vol % Each Methanol/TBA
- 1981 -- EPA Waiver Issued for 50/50 Methanol/TBA with 3.5 wt % Oxygen Maximum Limit
- 1981 -- EPA "Substantially Similar" Rule Issued with 2.0 wt % Oxygen Maximum Limit (11 vol % MTBE)
- 1987 -- Denver Begins Wintertime Oxygenated Gasoline Program Using MTBE (Later Ethanol Used)
- 1988 -- EPA Waiver Issued for 15 vol % Maximum MTBE
- 1989 -- Phoenix, Las Vegas, Reno, and Albuquerque Begin Wintertime Oxygenated Gasoline Program Using MTBE (Later Ethanol Used)

When Continued

- 1991 -- "Substantially Similar" Maximum Oxygen Limit Increased to 2.7 wt % (15 vol % MTBE)
- 1992 -- Federal Wintertime Oxygenated Gasoline Program Requiring 2.7 wt % Minimum Oxygen Begins in 39 Carbon Monoxide Nonattainment Areas
- 1995 -- Federal Reformulated Gasoline Program Requiring 2.0 wt % Minimum Oxygen Begins
- 1996 -- California Phase 2 Reformulated Gasoline Requiring 1.8-2.2 wt % Oxygen Begins

Properties of Alcohols

Property	Methanol	Ethanol	Isopropyl Alcohol	n-Butanol	Gasoline-Grade t-Butanol
Abbreviation	MeOH	EtOH	IPA	BuOH	GTBA
Autoignition Temperature, °F (°C)	867 (464)	793 (423)	750 (399)	-	892 (478)
Blending (R+M)/2 ^a	119	115	106	86	97
Blending Vapor Pressure, psi (kPa) ^b	40 (276)	18 (124)	14 (97)	9 (62)	9 (62)
Boiling Point, °F (°C)	149 (65)	173 (78)	180 (82)	244 (118)	176-181 (80-83)
Chemical Formula	CH ₃ OH	C ₂ H ₅ OH	(CH ₃) ₂ CHOH	C ₄ H ₉ OH	(CH ₃) ₃ COH
Coefficient of Thermal Expansion at 60°F (15.6°C), per °F (°C)	0.00067 (0.0012)	0.00062 (0.0011)	-	-	-
Composition, wt %					
Carbon	37.49	52.14	59.96	64.82	65.0
Hydrogen	12.58	13.13	13.42	13.60	13.7
Oxygen	49.93	34.73	26.62	21.58	21.3
Electrical Conductivity, mhos/cm	4x10 ⁻⁷	1.35x10 ⁻⁹	-	-	-
Flammability Limits, vol % vapor in air	7.3 to 36.0	4.3 to 19.0	2.0 to 12.0	1.4 to 11.2	2.4 to 8.0
Flash Point, °F (°C)	52 (11)	55 (13)	53 (12)	84 (29)	52 (11)
Heating Value, lower, Btu/gal (kJ/L)	56,800 (15,800)	76,000 (21,200)	87,400 (24,400)	96,800 (27,000)	94,100 (26,300)
Latent Heat of Vaporization, Btu/gal (kJ/L)	3340 (931)	2378 (663)	2100 (585)	1700 (475)	1700 (474)
Molecular Weight	32.04	46.07	60.09	74.12	73.5
Refractive Index, n _D at 68°F (20°C)	1.3286	1.3614	1.3772	1.3983	1.3838
Relative Density 60/60°F (15.6/15.6°C)	0.7963	0.7939	0.7899	0.8137	0.7810
Specific Heat, Btu/lb-°F (kJ/kg-°K)	0.60 (2.51)	0.57 (2.39)	0.81 (2.55)	0.58 (2.35)	0.72 (3.82)
Stoichiometric Air-Fuel Ratio, wt	6.45	9.00	10.3	11.1	11.1
Viscosity, mm/s					
68°F (20°C)	0.74	1.50	3.01	3.54	7.4
-4°F (-20°C)	1.44	3.58	7.43	-	Solid
Water Solubility, 70°F (21°C)					
Fuel in water, vol %	100	100	100	100	100
Water in Fuel, vol %	100	100	100	100	100

^a in 87 (R+M)/2 typical composition unleaded gasoline.

^b at nominally 10 vol %.

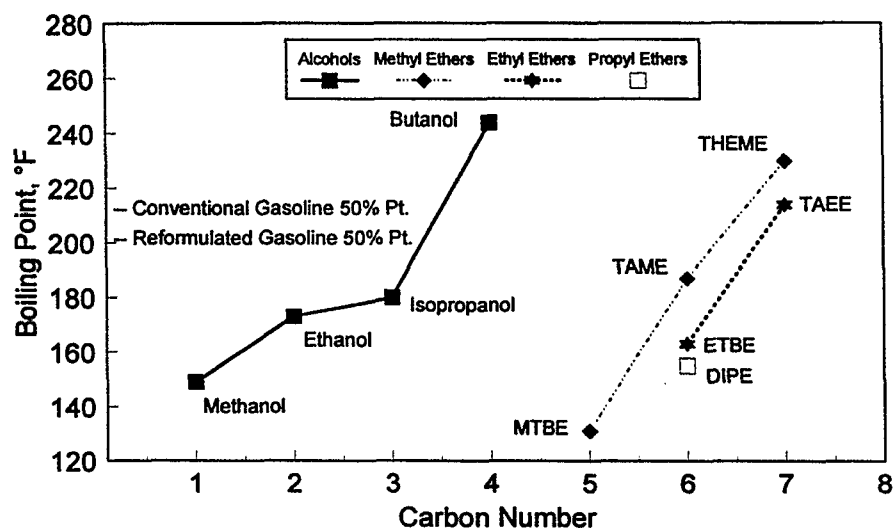
Properties of Ethers

Property	Methyl Tertiary-Butyl Ether	Tertiary-Amyl Methyl Ether	Tertiary-Hexyl Methyl Ether	Ethyl Tertiary-Butyl Ether	Tertiary-Amyl Ethyl Ether	Diisopropyl Ether
Abbreviation	MTBE	TAME	THEME	ETBE	TAE	DIPE
Autoignition Temperature, °F (°C)	815 (435)	-	-	-	-	830 (443)
Blending (R+M)/2 ^a	110	105	95	111	100	107
Blending Vapor Pressure, psi (kPa)	8 (55)	2 (14)	1 (7)	4 (28)	2 (14)	0.7 (5)
Boiling Point, °F (°C)	131 (55)	187 (86)	~230 (~110)	163 (73)	214 (101)	155 (68)
Chemical Formula	(CH ₃) ₃ COCH ₃	(CH ₃) ₂ (C ₂ H ₅)COCH ₃	(CH ₃) ₂ (C ₃ H ₇)COCH ₃ ^b	(CH ₃) ₃ COC ₂ H ₅	(CH ₃) ₂ (C ₂ H ₅)COC ₂ H ₅	(CH ₃) ₂ CHOCH(CH ₃) ₂
Coefficient of Thermal Expansion at 60°F (15.6°C), per °F (°C)	0.00078 (0.00143)	-	-	0.00077 (0.00140)	-	0.00080 (0.00144)
Composition, wt %						
Carbon	68.13	70.53	72.35	70.53	72.35	70.53
Hydrogen	13.72	13.81	13.88	13.81	13.88	13.81
Oxygen	18.15	15.66	13.77	15.66	13.77	15.66
Electrical Conductivity, mhos/cm	-	-	-	-	-	-
Flammability Limits, vol % vapor in air	1.6 to 8.4	1.0 to 7.1	-	1.0 to 6.8	-	1.4 to 7.9
Flash Point, °F (°C)	-14 (-26)	11 (-11)	-	-3 (-19)	-	9 (-12)
Heating Value, lower, Btu/gal (kJ/L)	93,500 (26,000)	100,600 (28,000)	-	97,000 (27,000)	-	100,000 (27,900)
Latent Heat of Vaporization, Btu/gal (kJ/L)	863 (241)	870 (243)	-	830 (232)	816 (228)	900 (251)
Molecular Weight	88.15	102.18	116.20	102.18	116.20	102.18
Refractive Index, n _D at 68°F (20°C)	1.3689	1.3760	-	1.3885	1.3912	1.3681
Relative Density 60/60°F (15.6/15.6°C)	0.7460	0.7758	0.7860	0.7452	0.7705	0.7289
Specific Heat, Btu/lb-°F (kJ/kg-°K)	0.50 (2.09)	0.52 (2.18)	-	0.51 (2.13)	0.50 (2.09)	-
Stoichiometric Air-Fuel Ratio, wt	11.7	12.1	12.5	12.1	12.5	12.1
Viscosity, mm/s						
68°F (20°C)	0.47	-	-	-	-	-
-4°F (-20°C)	1.44	-	-	-	-	-
Water Solubility, 70°F (21°C)						
Fuel in water, vol %	4.8	1.15	-	1.2	0.4	-
Water in Fuel, vol %	1.5	0.6	-	0.5	0.2	-

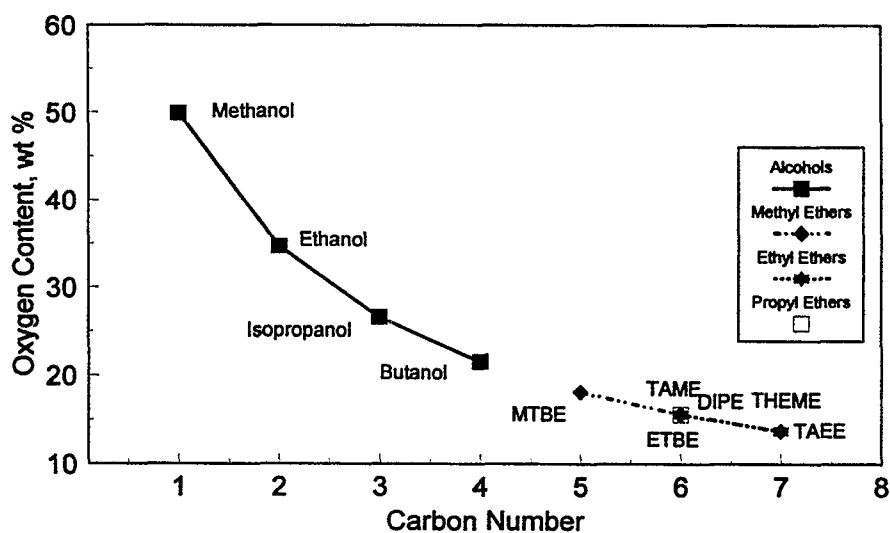
^a in 87 (R+M)/2 typical composition unleaded gasoline.

^b Most prevalent of four isomers.

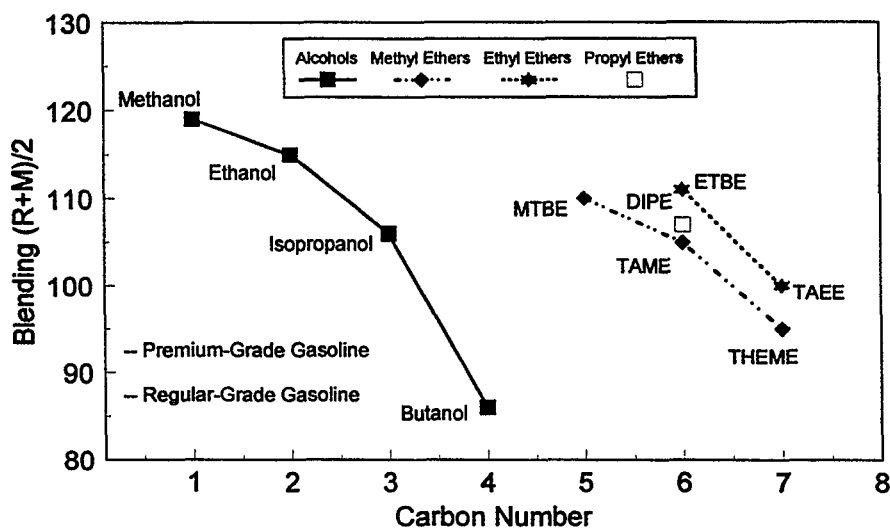
Effect of Oxygenate Carbon Number on Boiling Point



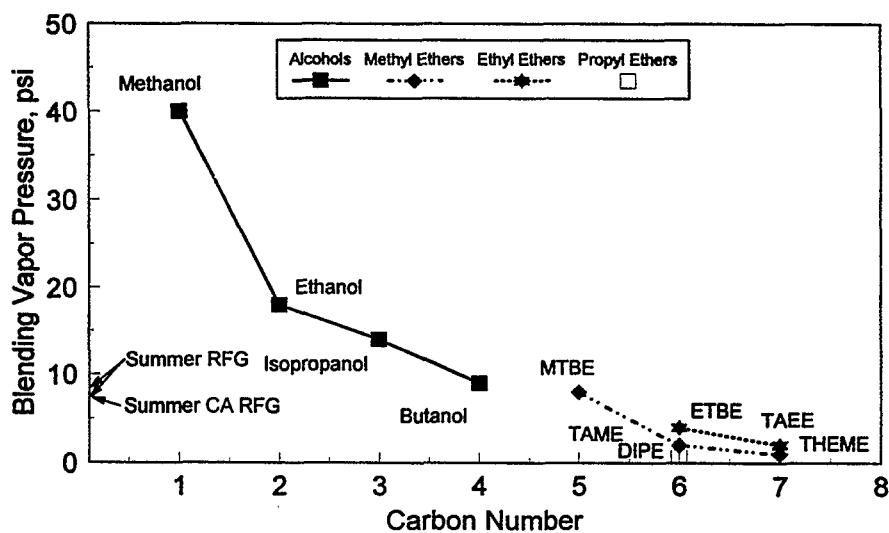
Effect of Oxygenate Carbon Number on Oxygen Content



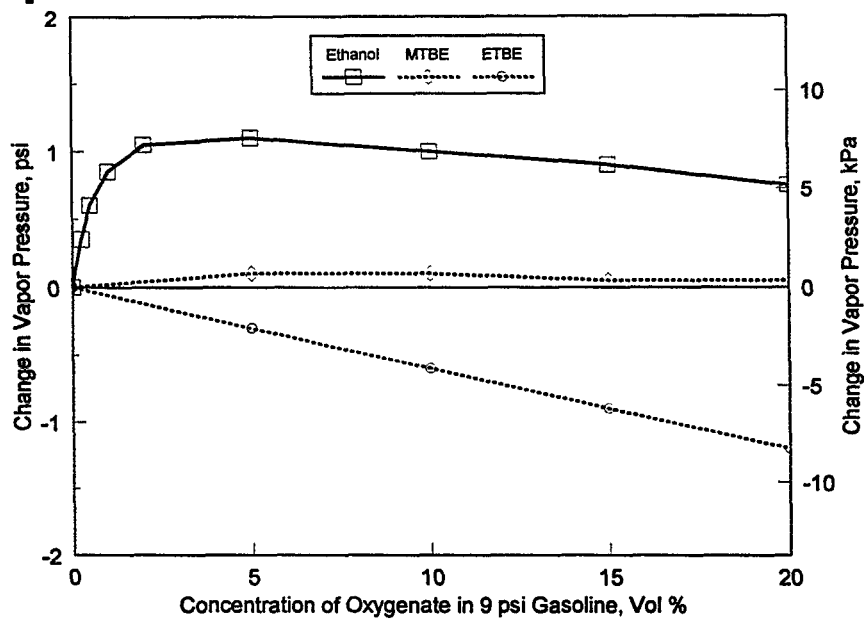
Effect of Oxygenate Carbon Number on Blending Antiknock Index, (R+M)/2



Effect of Oxygenate Carbon Number on Blending Vapor Pressure



Effect of Oxygenate Addition on Vapor Pressure



Why is MTBE Chosen Over Ethanol for Reformulated Gasoline?

- Less Effect on Vapor Pressure
- Superior Water Tolerance of Blend
 - Can be Refinery Blended
 - Can be Shipped in Pipelines, Barges, and Tankers
 - Doesn't Have to be Terminal Blended
 - Less Field Attention Required
- At Constant Oxygen Level, Provides More Dilution of:
 - Benzene
 - Aromatics
 - Olefins
- Made in Refineries/Chemical Plants and Easier to Transport
- Doesn't Require Subsidy to be Economic

Why is Ethanol Frequently Used for Wintertime Oxgenated Gasoline?

- Federal Vapor Pressure Regulations Not in Effect in the Wintertime
- Both Federal and State Tax Breaks Make it Economically Attractive
- Some State Regulations Require its Use (Maybe Indirectly by Setting the Minimum Oxygen Content Above the Maximum Allowed for MTBE)



Chevron Products Company

Getting Reliable Data from Water Labs Testing for MTBE (or any Other Volatile Contaminant)

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In order to protect the public water supply, sensitive and reliable analytical test methods are needed for use in compliance monitoring by utility laboratories. MTBE is a relatively new threat to the drinking water supply that has extremely low odor and taste thresholds and possible toxicity. The determination of MTBE in water is expected to be technically challenging and error prone for several reasons: i) MTBE is a cocontaminant with gasoline, a complex matrix of potentially-interfering components; ii) MTBE is "difficult to purge" due to its polarity and water solubility; iii) MTBE has become a common extraction solvent in water laboratories leading to a high potential for contamination in the lab; and iv) there is a significant potential for contamination of samples during sampling, transport and storage because of its high concentration in gasoline. Moreover, many environmental testing laboratories are relatively inexperienced in determining MTBE at this time and are not certified for testing MTBE *per se*.

The purpose of this presentation is to consider the technical challenges to the analytical chemist determining traces of MTBE in water. Sampling also is reviewed as no discussion of MTBE testing would be complete without acknowledging the problem of obtaining representative samples at the laboratory. Armed with this information consumers of laboratory test data will be better equipped to judge data quality and ensure that the data suits their requirements. In spite of its unique characteristics, many of the challenges in testing MTBE are common to all VOC.

Notes Pertaining to Attached Slides

Slide #1 Title slide

Slide #2 MTBE is one of various alkyl ether oxygenates discussed here including ETBE, TAME and DIPE. MTBE is added to gasoline at high levels (e.g. 11%) in order to increase the octane rating of the fuel as well as decrease the emission of primary pollutants, notably carbon monoxide. Because of the high level of addition to fuel MTBE is referred to as a blending agent. Additional fuel oxygenates are shown including ethanol and *tertiary*-butyl alcohol.

Due to its use patterns MTBE is a relatively new contaminant in ground and surface water. Accordingly, MTBE also is a new threat to drinking water supplies. Initial interest in monitoring drinking water for MTBE dates back to about 1992 with the publication of USEPA Method 524.2 (Revision 4), one of two approved methods for the determination of volatile contaminants in drinking water compliance monitoring. MTBE was one of 24 volatile target compounds added to this gas chromatography-mass spectrometry (GC-MS) method.

Our laboratory is the primacy laboratory for California's drinking water program. Our interest in analysis of MTBE dates back to publication of Revision 4. Over the past 3 years the laboratory has been active in determining MTBE and other oxygenates in drinking water as well as a surface and ground water.

Slide #3 MTBE has various properties that enhance the potential for groundwater contamination including high water solubility, low biodegradation potential and low sorption characteristics. While these environmental characteristics enhance the potential for contamination of drinking water supplies, the overriding factors leading to contamination are the tremendous production volumes and the number of mobile and stationary sources.

Slide #4 MTBE and the other fuel oxygenates are likely candidates for increased regulation in drinking water for various reasons including those noted.

Slide #5 While MTBE can readily be determined by purge and trap (P & T) gas chromatography (GC) methods including GC-MS, the determination of MTBE is more challenging than many other volatile organic compounds (VOC) for various reasons. First, MTBE is a cocontaminant with a petroleum product, gasoline, which is itself a complex chemical mixture. Thus, occurrence of this complex mixture increases the possibility of qualitative and quantitative errors in MTBE determination. MTBE is a polar compound that has relatively low purge efficiency. Thus, other VOC may be completely stripped from water while only a portion of the MTBE is recovered using the standard P & T conditions. This can lead to quantitation errors. Because MTBE is a major gasoline component there is tremendous potential for contamination of

water samples in the field, and during transport of samples back to the laboratory. MTBE has become a common extraction solvent in water testing laboratories over the past 5 years increasing the potential for contamination of samples in the lab. Even methanol, widely used in the methods for determination of VOC, is frequently contaminated with MTBE (personal communication, J. Munch, USEPA).

Slide #6 Objectives of presentation

Slide #7 Getting representative samples back to the laboratory is probably the single greatest challenge in testing water for MTBE or other VOC. This slide provides a brief overview of the standard techniques for good VOC sampling. Anyone responsible for water sampling should be thoroughly familiar with these precautions which are outlined in more detail in USEPA drinking water test methods.

The purpose of these controls is to avoid false positives and false negatives and to ensure that the concentrations of MTBE determined in the laboratory are representative of the water supply at the time of sampling. MTBE and other VOC do not remain dissolved in water, especially shallow water, for long. Thus, VOC are always sampled using volatile organic analysis (VOA) vials which are the appropriate volume (40 mL) and are well sealed with a Teflon®-lined closure. The vial is filled so that the meniscus is above the top of the vial – when the sealed sample is inverted there should be no air bubbles. The laboratory should reject any samples received with more than a pea-sized air bubble (or flag the data). Because VOC are ephemeral in water they should be returned to the laboratory as soon as possible, ideally within 24 hours of sampling, but certainly within the 14-day holding time. Preservation is critical including low temperature storage and adjustment of the pH with hydrochloric acid. Adjustment of pH can be carried out in the field safely by use of plastic dropper bottles containing 1:1 hydrochloric acid (personal communication, R. Hine, State of New Mexico, Department of Health). Any residual chlorine in the water must be removed by addition of a reducing agent such as thiosulfate or ascorbate.

A minimum quality assurance program must include positive and negative controls. Travel blanks must accompany the empty sample containers to the field. On leaving the laboratory they are filled with laboratory reagent water which is free of detectable chemical contamination. If low recoveries are suspected, reagent water can be fortified with MTBE at a concentration near the reporting limit – these laboratory-fortified blanks (LFBs) also accompany the sample vials. Duplicates are necessary for each and every source due to pervasive problems in VOC sampling. The holding time, the time between filling the VOA vial and processing the sample in the instrument, is 14 days. During the holding time the sample vial remains sealed and is kept at 4°C. VOC samples should not be transported or stored in the vicinity of gas cans, paints, solvents, or highly contaminated samples.

Slide #8 Understanding and measuring detection limits in drinking water labs is a recurring problem. In drinking water monitoring detection limits are based on the method detection limit (MDL). This diagram explains the conceptual model for detection limits. Regardless of the concentration of analyte present, the analytical instrument gives a signal shown here as a normal distribution. The objective is to locate the signal intensity at which there is very low probability that the concentration is actually zero. The MDL is that concentration.

Slide #9 The USEPA has published a standardized technique for determination of MDLs in the Federal Register. This protocol is well known to chemists in drinking water laboratories. Highly purified laboratory water is spiked at very low concentrations with the analyte of interest. The MDL is the product of the standard deviation of seven determinations and a t-statistic.

A very important point for laboratory users to be aware of is that reliable detection does not mean reliable quantitation. Quantitation errors are quite large near the detection limit and in the interest of reporting only reliable data laboratories set the reporting limit at some multiple of the MDL.

Drinking water laboratories must repeat their determination of the MDL on a yearly basis because MDLs vary with many factors including time, instrument, chemist, and even the way in which the MDL was measured. To ensure that your laboratory is adhering to good laboratory practices request data from the most recent MDL study. Moreover, reporting limits should be listed and their basis explained.

Slide #10 MTBE and the other fuel oxygenates (DIPE, ETBE and TAME) can be determined using P & T GC methods. While USEPA has not published information on the determination of these compounds using USEPA Method 502.2, the approved GC method for determination of VOC in drinking water, the method appears to be satisfactory for this purpose. Linear calibration curves for the 4 oxygenates are shown using the photoionization detector or PID. The alkyl ether oxygenates give no response to the electrolytic conductivity detector, which responds to halogens. Therefore, determining oxygenates by Method 502.2 is not as reliable as determination of halogenated aromatics and olefins, for example, because confirmatory detection is not possible.

Slide #11 GC determination of the alkyl ethers by Method 502.2 is accurate at low concentrations and the MDLs are very low, well below the legal reporting requirement for most VOC monitored in California drinking water, 0.5 µg/L.

Slide #12 A major pitfall in determination of VOC by gas chromatography is that retention times drift. This leads to wide windows and poor specificity. Thus, GC methods are prone to errors in identification, a problem compounded by the presence of petroleum. Some of the petroleum contaminants like 2- and 3-methylpentane also respond to the PID and have retention times similar to MTBE.

Slide #13 Mass spectrometry can provide more reliable determination of MTBE because it bases identification not only on the retention time of the analyte, but also mass spectral features of the peak. Mass spectrometry theory is beyond the scope of this paper, but it suffices to say that each and every chemical in the mass spectrometer has a specific "signature." The signatures of many thousands of chemicals are compiled in the mass spectrometer's computer library. Modern instruments are able to quickly confirm that the peak tentatively identified as MTBE has not only the correct retention time, but also the correct spectroscopic features.

Slide #14 This table lists the target compounds from USEPA Method 524.2 that have retention times similar to the alkyl ether oxygenates. The column used was a 60-meter VOCOL column (for any chemists happening upon this paper). There are several resolution challenges including, for example, MTBE/acrylonitrile, DIPE/1,1-dichloroethane, and ETBE/2,2-dichloropropane, and benzene/TAME. It would be difficult to confuse these analytes, however, since the mass spectra are unique. Spectroscopy, thus, adds a further dimension on which to "separate" the sample constituents.

Slide #15 What about confusing the alkyl ether oxygenates with gasoline components? Even though these materials are similar in retention time, the spectra allow distinction. Because of the substantial improvement in specificity of GC-MS over GC methods for MTBE in water, it is highly recommended that GC detections be confirmed by mass spectrometry.

Slide #16 GC-MS methods performed properly and with the necessary quality controls, afford high sensitivity and accuracy in the low parts-per-billion concentration range. Based on these data a laboratory reporting limit of 1 to 3 µg/L would be appropriate. As noted above MDLs vary with spike level, instrument, operator, instrument condition, etc. Under typical use conditions (e.g., day-to-day lab operation) the MDL may be an unrealistically low estimate of lab detection capability.

Slide #17 MDLs vary with spike concentration among other things (for more information see W. Draper et al, AWWA Journal, June, 1998).

Slide #18 ETBE, TAME and DIPE also are determined reliably using USEPA Method 524.2 with low detection limits and high accuracy.

Slide #19 The remaining slides deal with specific problems or pitfalls that can be encountered in determination of MTBE. These examples were taken from testing done in our laboratory over the past 3 years.

In this table are results of the analysis of drinking water samples from a small water system in a rural community. This site had historic contamination from leaking underground fuel tanks and recent complaints regarding petroleum-like taste and odor in the water. While this level of contamination is extremely unusual in drinking water testing, it is probably encountered frequently in LUFT investigations. MTBE concentrations are about 10,000 times the detection limit. This leads to various problems in low-level chemical analysis such as poor accuracy and false positives. The next sample can be contaminated with 1-5% carryover.

In order to meet the sensitivity requirements for drinking water compliance monitoring a 25-mL sample is purged. Analysis of 25-mL samples, however, saturates the instrument and gives a response outside the calibration range. In this case analysis of a smaller sample volume (e.g., 5-mL) gives a more accurate result for both MTBE and benzene.

Slide #20 Reducing the sample size, however, cannot be done without increasing the reporting limits for the other contaminants in the sample. In this case highly contaminated ground water from a brownfield site near Signal Hill (CA) contains high levels of BTEX and MTBE. To improve the accuracy of the analysis the sample size is reduced by using a lower volume (5 vs. 25 mL) and by dilution of the sample with laboratory reagent water. Reducing of the sample volume and diluting the sample each result in higher and higher reporting limits. Even after analysis of the sample three times the reporting limit for ethyl benzene is 12.5 µg/L. To meet the mandatory reporting limits for all of the contaminants and determine MTBE and the other high-level contaminants accurately requires a tremendous amount of time.

Slide #21 High level samples cannot be analyzed with low-level samples because of the problem of carryover. The components of the purge and trap apparatus cannot be completely decontaminated before introduction of the next sample. While 1-5% carryover is not a problem with typical drinking water samples, carryover and false positives are expected to occur in testing at LUFT sites, especially if reporting limits in the low parts-per-billion range are expected and the proper quality controls aren't employed. The table summarizes results of reagent blanks analyzed in a batch of BTEX samples from the Signal Hill site described above. False positives for benzene and toluene well above our reporting limits of 0.5 µg/L are seen (#3, #4, #5). Although the #s are sequential the blanks were distributed widely in the sample queue. Many reagent water blanks must be added to the sample queue to clean up the instrument and document that the system is clean. Again this consumes instrument time.

Slide #22 Another subtler problem associated with analysis of low and high level samples is particular to MTBE. For accurate quantitation MTBE must be calibrated under conditions identical to those used in sample analysis.

In this example our laboratory was submitted PE samples formulated at our Southern California laboratory – the formulation is shown in the last column. Our laboratory was submitted the samples blind and asked to report BTEX and MTBE. Analysis of 25-mL samples and 5-mL samples gave very different MTBE results although there is good agreement in the case of the other analytes.

The origin of this of this discrepancy is that MTBE purge efficiency is dependent on the sample volume. The efficiency is higher when a lower volume is purged. In this case we calibrated the instrument with 25-mL samples – results of the analysis of the 5-mL samples have a positive bias. Note that the surrogates added to the sample, bromofluorobenzene and deuterated dichlorobenzene, also indicate a bias problem when 5-mL samples are analyzed. The bias is far more pronounced in the case of MTBE, which has poor purge efficiency due to its polarity.

Slide #23 The correct way to reduce the sample size is to dilute the sample with reagent water, not just lower the volume. The technical point again is that the instrument must be calibrated under identical conditions to those used in sample analysis. Either the sample volume must be held constant or two calibration curves are needed to accommodate both 5 and 25-mL samples.

Slide #24 As noted above gas chromatography methods operated properly can be used in screening water for MTBE. In this example surface water from a reservoir was analyzed by both P & T gas chromatography (Method 502.2) and P & T GC-MS (Method 524.2). Our laboratory analyzed the samples in order to resolve conflicting results from private water testing laboratories used by the utility. MTBE was reported by one laboratory but not the other.

These comparative data demonstrate a number of points. First, the reservoir was indeed contaminated with MTBE and the mass spectrometry data confirm detection by gas chromatography. This is not surprising as the reservoir had multiple uses including recreational boating and use of 2-cycle outboard motors. Second, both analytical methods can provide comparable quantitative results. In this case based on the analysis of commercial reference materials the GC method appears to be slightly more accurate than the GC-MS. This is not a general observation, however, and is simply due to a single comparison of the two methods. Finally, differences in reporting limits or reporting policy explain many discrepancies when splits are analyzed. At the time these samples were analyzed the mandatory reporting limit for drinking water monitoring (the California DLR) was 5 µg MTBE/L. MTBE concentrations in the reservoir are in the same range as the DLR. Thus, the discrepancy could be attributed to experimental error or even differences in reporting limits at the two labs.

Reporting limits used by the laboratory should be clearly stated. Moreover, when multiple laboratories are used the reporting policy needs to be consistent and based on the same criterion, e.g., the same multiple of the MDL, the DLR or some other equivalent value.

Comparability of data between laboratories is very difficult to achieve, but experience has shown that comparability improves when the same analytical methods are used at the two laboratories. In drinking water monitoring the approach has been to require the use of the approved, prescriptive methods. Much more latitude has been allowed in LUFT testing in the past.

Slide #25 People who rely on laboratories for information need to appreciate the difference between raw instrument data and validated data. A common misconception is that sophisticated analytical instruments like mass spectrometers are fool proof, or that automation has minimized the importance of skilled operators. In fact automation has increased the importance of data validation and interpretation by skilled chemists.

In this table data from the analysis of surface water again is summarized. Water samples from a marina near Lake Tahoe were analyzed for petroleum-related residues including BTEX and MTBE. Contamination at the site was not surprising due to the amount of boat traffic, the appearance of a film on the water, and the odor of MTBE in the area. The MTBE and BTEX concentrations found in the laboratory were above the drinking water DLRs (0.5 µg/L for BTEX compounds and 5 µg MTBE/L).

Raw data from the mass spectrometer provided erroneous information including false positives (acrylonitrile and trimethylbenzene), false negatives (naphthalene and propylbenzene) and quantitation errors (ethylbenzene). Only when an experienced chemist examined the raw data were these errors apparent. The principal problem was relatively simple in that the retention times of the analytes had drifted during analysis of sample batch. Simply updating the information on retention times eliminated many of the errors. Other errors were uncovered by visual comparison of the sample spectra and spectra of standards.

As a detector for gas chromatography the mass spectrometer looks in retention time windows for spectra which satisfy a particular match or fit. In order to optimize the sensitivity of the instrument the fit criteria may be relaxed. The mass spectrometer data system ascertains only that a threshold is exceeded in identifying detections or hits. While computerized data systems have attained remarkable processing speed, the fundamental programs or algorithms on which spectra are compared and judged equivalent continue to have limitations. Mass spectrometry itself is often incapable of distinguishing isomers, e.g., the signatures of *ortho* and *meta* xylenes may not be distinguishable, and in these cases the retention time of the unknown is critical.

Thus, while mass spectrometry is an extremely specific technique for detection of VOC it is not infallible. Raw mass spectrometry data requires detailed review and examination by a skilled spectroscopist before reliable information is attained. This review cannot be automated and therefore is a very costly component of the analysis.

Slide #26 Obtaining reliable data from laboratories requires a substantial amount of laboratory work beyond instrumental analysis of the water sample itself. This table shows the queue of analyses required in the determination of volatile organic compounds in just two water sources. The last column explains the reason or purpose for each. Only with this level of effort can false positives and negatives be avoided. Included in this list are so-called QC samples which are more widely known as reference materials which have a known or established composition as well as acceptance limits for analysis results. Successful analysis of the reference material demonstrates that the laboratory has satisfied a standard of accuracy against an external yardstick.

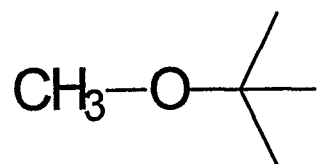
Slide #27 Those relying on water testing laboratories for information face one overriding concern, that almost all of things needed to ensure quality reduce the throughput of samples. They involve a substantial cost in instrument time or analysis cycles required. In the case of testing water for volatiles such as MTBE this typically means doubling or tripling the number of determinations. The labor costs involved are proportional to the number of cycles. There is tremendous value added to the data when experienced chemists take the time to examine the raw data carefully.

The pie chart shown emphasizes the importance of labor costs in environmental testing. And because many of the other costs are considered to be fixed, there is tremendous pressure to decrease the time allotted to reviewing laboratory test data. While the purpose of this is to consider technical issues, economics can't be overlooked. It has been reported in trade literature that the environmental laboratory testing business has become extremely competitive. The cost of BTEX analysis declined 14% between 1995 and 1996 and the cost fell a further 3.2% between 1996 and 1997 according to a report in Environmental Testing and Analysis (March/April, 1998). Increased efficiency should not be confused with skimping on the quality control program. Laboratory users need to ensure that all of the elements of the quality control program are present and recognize that every aspect of the laboratory work has a cost associated with it.

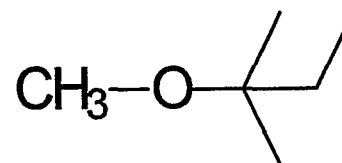
Slide #28 Conclusion slide

Getting Reliable Data from Water Labs Testing for MTBE (or any Other Volatile Contaminant)

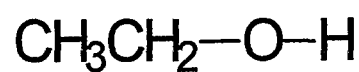
Current Fuel Oxygenates



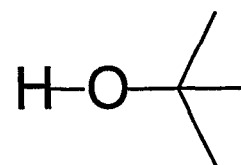
MTBE



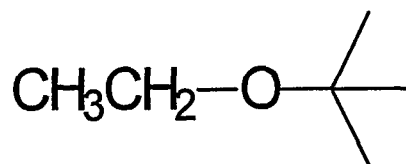
TAME



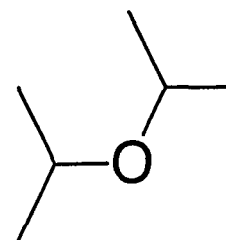
Ethanol



TBA



ETBE



DIPE

Properties of alkyl ether oxygenates

- Highly soluble in water
- Less biodegradable than other gasoline components (e.g., BTEX)
- Weakly sorbed to soils and aquifer materials

Fuel Oxygenates are Candidates for Regulation

- Low Taste and Odor Thresholds
- MTBE appears in SDWA's Drinking Water Priority List
- MTBE appears as a new target compound in compliance monitoring methods for drinking water

Challenges in MTBE Determination

- Occurs with complex mixture
- Difficult to purge
- Common extraction solvent
- Potential for contamination in field

Objectives

- Review sampling technique
- Discuss purge & trap GC and GC-MS methods for MTBE and other oxygenates
- Consider specific pitfalls in MTBE testing

Sampling, Preservation, Transport, Storage Guide

- Use VOA vials
- Get to lab in 24 hrs
- Preserve
 - 4°C
 - pH < 2
 - Remove chlorine
- Use Travel blanks
- Use Travel LFBs
- Analyze Duplicates
- Observe holding time
- Don't store in hot trunk with gas can

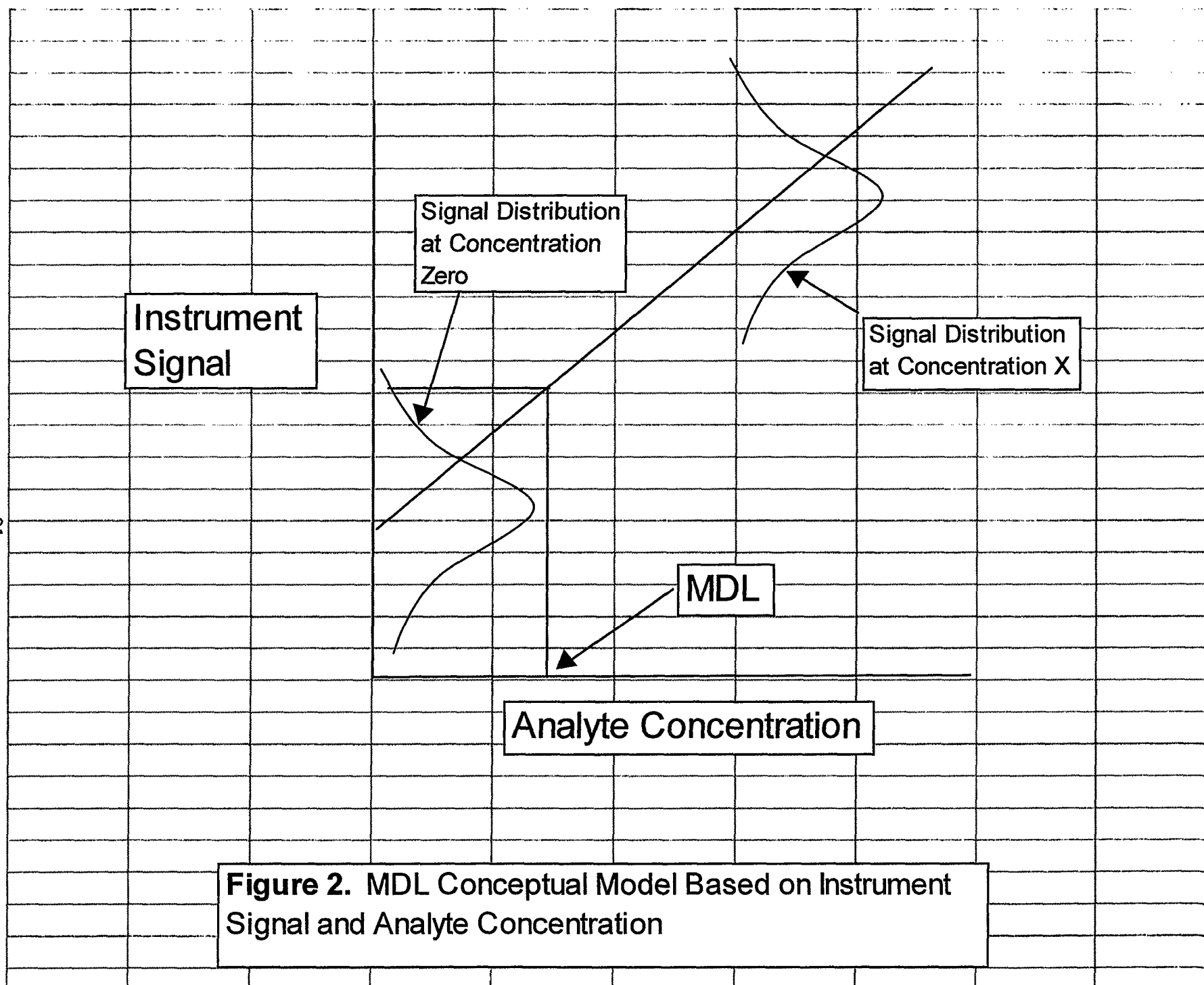
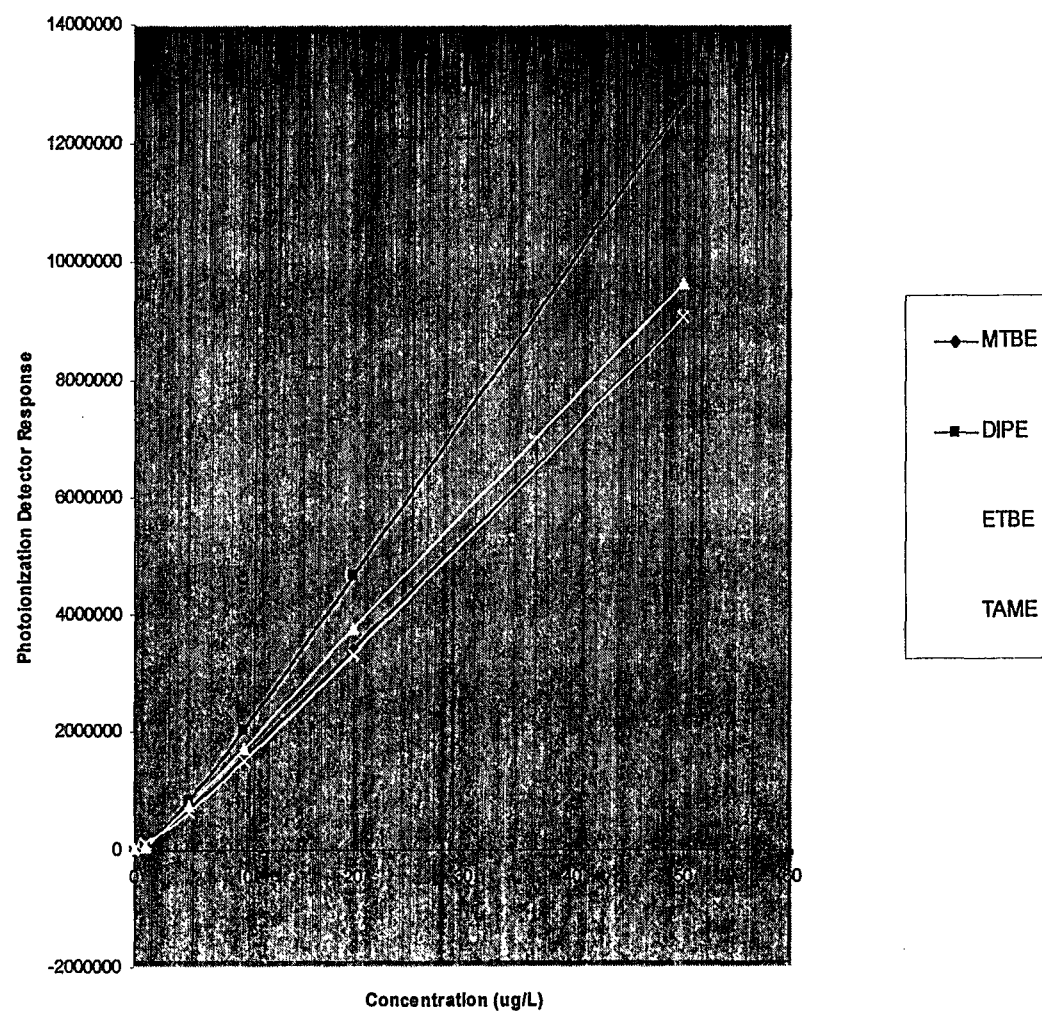


Figure 2. MDL Conceptual Model Based on Instrument Signal and Analyte Concentration

Determination of MDL

- Spike Purified Water with Low Concentrations
- Analyze Seven Replicates
- $MDL = 3.143 \times \text{standard deviation}$
- **Reporting Limit is 3-10 X MDL**

Fuel Oxygenates by Method 502.2



	Accuracy @ 0.5 ug/L			
Experiment	MTBE	DIPE	ETBE	TAME
Fuel Oxygenates Only	81%	84%	92%	82%
Oxygenates & Other VOC	82%	86%	86%	53%
	MDL @ 0.5 ug/L			
Experiment	MTBE	DIPE	ETBE	TAME
Fuel Oxygenates Only	0.2	0.08	0.2	0.2
Oxygenates & Other VOC	0.1	0.05	0.07	0.05

Windows for Selected Oxygenates				
Oxygenate	Retention Time (Minutes)			
	Average	SD	Window	
MTBE	19.41	0.28	18.57	20.25
DIPE	21.16	0.27	20.35	21.97
ETBE	22.73	0.27	21.92	23.54
TAME	26.89	0.27	26.08	27.7

How Are Oxygenates Identified?

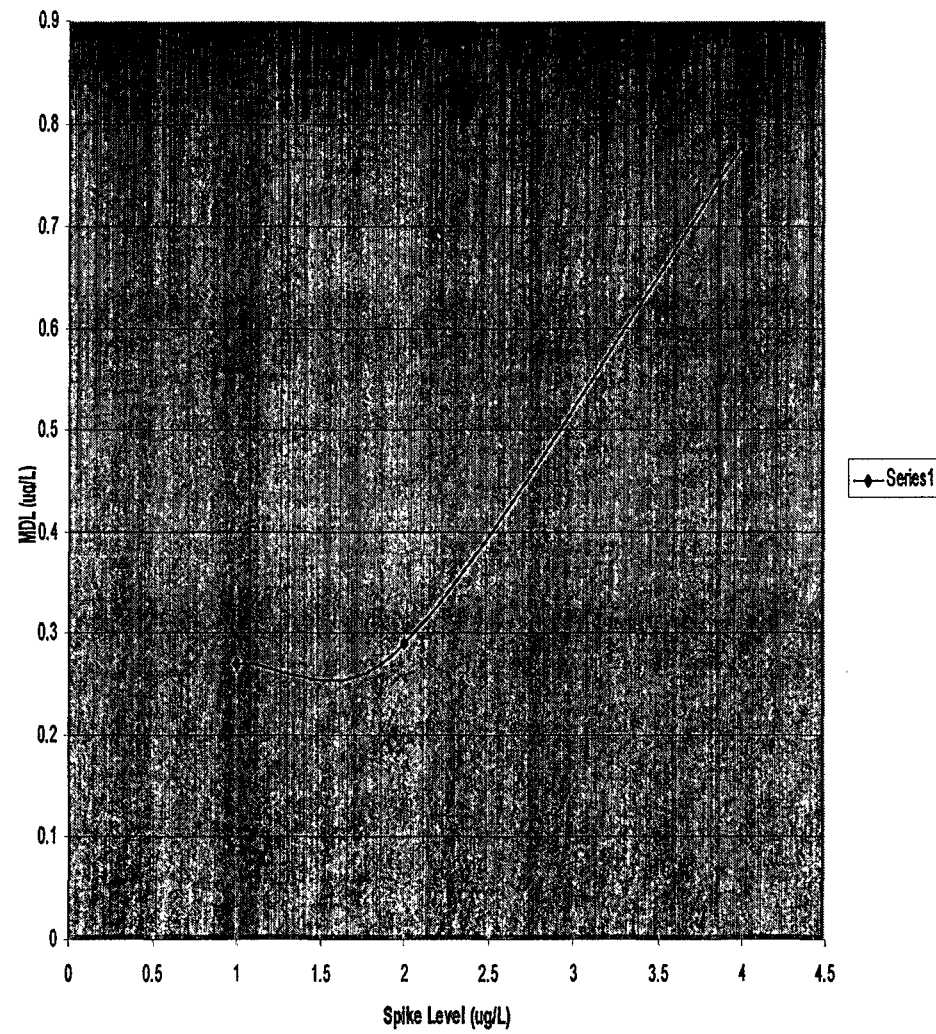
- GC Method:
 - Retention Time
- GC-MS Method:
 - Retention Time
 - Characteristic MS Ion(s)
 - Computerized Library Search & Spectral “fit”
 - Comparison of Library/Sample Spectrum

Alkyl Ether Oxygenate Neighbors		
Target Compound	tR (Min)	Ions (m/z)
Allyl chloride	7.45	41
Carbon disulfide	7.6	76
Methylene chloride	8.05	49
MTBE	8.53	73, 41, 57
Acrylonitrile	8.72	53
t-1,2-Dichloroethene	8.77	98
DIPE	10.12	45, 43, 87
1,1-Dichloroethane	10.17	63
ETBE	11.38	59, 87, 57
2,2-Dichloropropane	11.53	77
2-Butanone	11.97	43
c-1,2-Dichloroethene	12.1	61
Chlorobutane	13.95	56
1,1-Dichloropropene	14.45	75
Carbon Tetrachloride	14.38	117
TAME	14.85	73, 55, 87
Benzene	15.08	78
1,2-Dichloroethane	15.3	62

Alkyl Ether Oxygenate Neighbors		
Target Compound	tR (Min)	Ions (m/z)
2-methylpentane	7.5	43, 42, 71, 57
3-methylpentane	8.13	57, 56, 41, 84
MTBE	8.53	73, 41, 57, 56
DIPE	10.12	45, 43, 87
ETBE	11.38	59, 87, 57
TAME	14.85	73, 55, 87
Benzene	15.08	78

MTBE MDL Study Data				
Spike level	Concentration (ug/L)			
	Mean	Accuracy	S.D.	MDL
1	0.89	89%	0.088	0.27
2	1.85	93%	0.093	0.29
4	3.39	85%	0.25	0.78

MTBE Method Detection Limit and Spike Level



MDLs, Spike Level and Pooled MDLs

Analyte	MDL @ 0.5 ug/L	MDL @ 1 ug/L	F-ratio
ETBE	0.09	0.2	3.74
TAME	0.1	0.2	4.19
DIPE	0.08	0.2	3.83

	MTBE (ug/L)		Benzene (ug/L)	
Sample	25 mL Sample	5 mL Sample	25 mL Sample	5 mL Sample
Well Head	Saturated	2,300	Saturated	270
Apartment Sink Tap	Saturated	1,800	Saturated	140
Store Sink Tap	Saturated	1,800	Saturated	82

	Concentration (ug/L) (5 mL Sample)			
Contaminant	Diluted 1 to 100	Diluted 1 to 10	Diluted 1 to 5	Report
Benzene	6,500	4,300	Saturated	6,500
Toluene	6,100	5,500	Saturated	6,100
Ethyl Benzene	<250	<25	<12.5	<12.5
MTBE	180	230	240	240

	Concentration (ug/L)				
Contaminant	5 mL Sample		25 mL Sample		Formulation
MTBE	2200	2400	1300	1100	1000
benzene	1.90	2.00	2.10	2.00	2.00
toluene	1.90	2.00	2.50	2.30	2.00
<i>ortho</i> -xylene	1.30	1.20	1.30	1.20	2.00
bromofluorobenzene	128%	135%	98%	98%	-
d4-1,2-dichlorobenzene	143%	153%	91%	88%	-

	Concentration (ug/L)		
Contaminant	5 mL Sample	5 mL Sample + 20 mL Reagent Water	25 mL Sample
MTBE	2100	810	1100
benzene	1.40	1.80	1.20
toluene	1.20	1.90	1.20
<i>ortho</i> -xylene	1.00	1.10	0.70
bromofluorobenzene	140%	98%	103%
d4-1,2-dichlorobenzene	160%	95%	95%

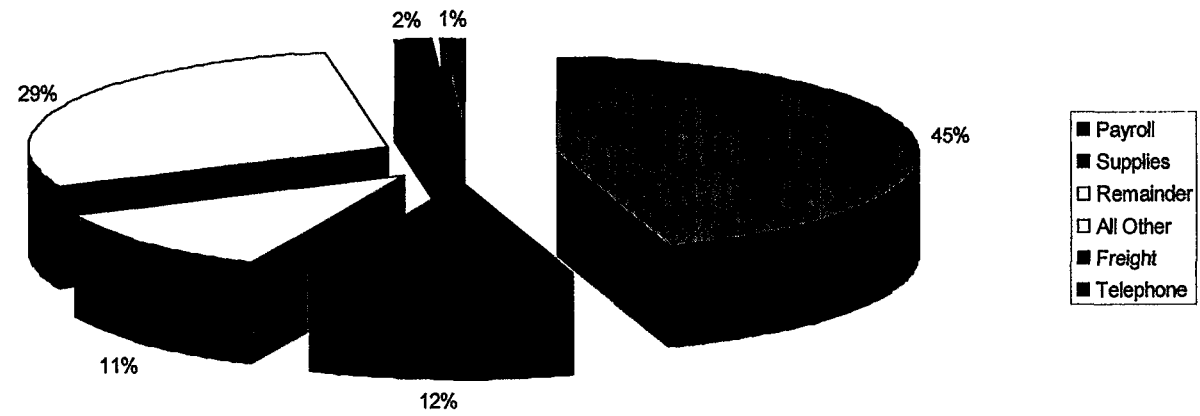
	MTBE Concentration (ug/L)	
Sample	USEPA Method 502.2	USEPA Method 524.2
Laboratory Reagent Blank	<0.25	<0.5
EBMUD Source Reservoir	5.2, 6.3, 5.4	4.2, 3.9, 4.2
Ultrascientific QC (10 ug/L)	9.7, 9.7	9.0, 9.1
Accustandard QC (10 ug/L)	9.9, 9.9	9.7, 8.3

Lake Tahoe Area Samples: Raw and (Real) Data					
	Parts Per Billion				
Contaminant	Boat Dock	Boat Dock	Marina	Marina	Problem
MTBE	72	71	21	20	No
Toluene	25	24	2.1	7.5	No
m + p Xylene	20	17	ND	5.2	No
o-Xylene	9.5	7.8	0.9	2.3	No
Benzene	6.2	5.7	1.5	1.8	No
Styrene	0.7	0.6	ND	ND	No
1,2,4-Trimethylbenzene	5.4	5.1	ND	1.4	No
Ethylbenzene	25(3.5)	23(3.3)	1.1(ND)	6.4(1.2)	Positive
Acrylonitrile	15(ND)	13(ND)	4.9(ND)	5.2(ND)	Positive
1,3,5-Trimethylbenzene	7.7(ND)	6.9(ND)	ND	0.5(ND)	Positive
Tetrahydrofuran	4.3(ND)	4(ND)	2.4(ND)	ND	Positive
2-Chlorotoluene	0.9(ND)	0.8(ND)	ND	ND	Negative
Naphthalene	ND(1.8)	ND(1.6)	ND	ND	Negative
n-Propylbenzene	ND(1.7)	ND(1.6)	ND	ND	Negative

GC-MS Queue for Analysis of VOC in Two Wells

#	Sample	Why Necessary
1	Water Blank	Demonstrates that system is clean
2	Calibration Standard 0.5 ug/L	Is system sensitive and what is linear dynamic range?
3	Calibration Standard 2 ug/L	
4	Calibration Standard 4 ug/L	
5	Calibration Standard 10 ug/L	
6	Calibration Standard 16 ug/L	
7	Calibration Standard 20 ug/L	
8	Calibration Standard 40 ug/L	
9	Water Blank	Cleans system
10	QC Sample	Tests accuracy relative to other laboratories
11	QC Sample	
12	Water Blank	Cleans system
13	QC Sample (Unregulated Analytes)	Tests accuracy relative to other laboratories
14	QC Sample (Unregulated Analytes)	
15	Water Blank	Cleans system
16	Calibration Standard 10 ug/L	Checks calibration
17	Water Blank	Cleans system
18	Water Blank	Cleans system
19	Travel Blank (SRL#98-553-1)	Looks for contamination in sampling, storage and lab
20	Corporation Yard Well #1 (SRL#98-549-1)	Provides information on well #1
21	Corporation Yard Well #1 (SRL#98-550-1)	
22	Corporation Yard Well #2 (SRL#98-551-1)	Provides information on well #2
23	Corporation Yard Well #2 (SRL#98-552-1)	
24	Water Blank	Cleans system

Environmental Laboratory Costs



Conclusions

- MTBE and other oxygenates are determined by purge & trap GC and GC-MS methods
- Proper sampling technique is critical
- All of the technical challenges can be addressed with proper quality controls
- QC is labor intensive and costly

MTBE Treatment and Remediation: An Overview of Alternative Technologies

Presented at the
Southwest Focused Ground Water Conference
on MTBE and Perchlorate

National Groundwater Association

June 3 - 4, 1998
Anaheim, California

Michael C. Kavanaugh, Ph.D., P.E., D.E.E.
Vice President

Andrew Stocking
Project Engineer

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Current Misconceptions About MTBE Treatment

- ▲ MTBE impossible to remove from water
- ▲ MTBE removal from water as difficult and as expensive as desalination of water
- ▲ Remediation of MTBE-impacted soil/groundwater will cost 30X that of BTEX-impacted soil/groundwater
- ▲ MTBE will persist and accumulate in surface waters

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Current Research Efforts Demonstrate Effectiveness of Existing and New Technologies to Remove MTBE from Soil/Water

- ▲ Research Partnership -- ACWA, WSPA, OFA, City of Santa Monica
- ▲ Demonstration Projects -- City of Santa Monica
- ▲ API Research
- ▲ University of California Studies
- ▲ Other Active Industrial/University Research -- Port Hueneme, Arizona State, equipment manufacturers

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Range of MTBE Treatment Challenges

Concentration Range (ppm)	Influent Level Scenarios	Volume Range (gpm)
Up to 40,000	▲ Refinery Spill	10 - 200
10 - 1,000	▲ Underground Tank Leak - Source	10 - 50
0.01 - 1	▲ Underground Tank Leak - Plume	25 - 200
0.01 - 1	▲ Drinking Water Treatment	200 - 5,000
0.02	▲ Surface Water Treatment	200 - 10,000

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Range of MTBE Treatment Challenges: Treatment Goals

- | | |
|------------------------------|-----------------------|
| ▲ Discharge to POTW | 0.1 - 1.0 ppm |
| ▲ Discharge to Surface Water | 0.1 - 10 ppm |
| ▲ Re-injection | 0.005 - 0.1 ppm |
| ▲ Drinking Water | ND (0.001) - 0.02 ppm |

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Technical Options: MTBE Remediation/ Treatment

- ▲ Phase Transfer
- ▲ Transformation / Destruction

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Technology Selection: Key Factors

- ▲ Effectiveness
- ▲ Residuals and By-product Formation/Control
- ▲ Process and Mechanical Reliability
- ▲ Ease of operation / Control / Implementation
- ▲ Permitting
- ▲ Public Acceptability
- ▲ Compatability
- ▲ Life Cycle Costs

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In-Situ Treatment and Remediation Technology Matrix: Soil and Groundwater

Phase Transfer

- ▲ Soil Vapor Extraction (SVE)
- ▲ Soil Heating/SVE
- ▲ Water Flushing
- ▲ Air Sparging/SVE
- ▲ In-well Aeration (NOVOCs)
- ▲ Steam Flushing

Transformation/Destruction

- ▲ Aerobic Biodegradation
 - MTBE as carbon source
 - cometabolism
- ▲ Chemical Oxidation
 - Hydroxyl Radicals
- ▲ Thermal Oxidation
 - Hydrous pyrolysis / oxidation

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MTBE Treatment and Remediation Ex-Situ Technology Matrix: Water and Air

Phase Transfer

Destruction

Water

- ▲ Air Stripping
- ▲ Activated Carbon
- ▲ Membranes
- ▲ Liquid / Liquid Extraction

- ▲ Oxidation (chemical)
- ▲ Aerobic Biodegradation

Air

- ▲ Activated Carbon
- ▲ Membranes

- ▲ Oxidation (thermal and chemical)
- ▲ Aerobic Biodegradation

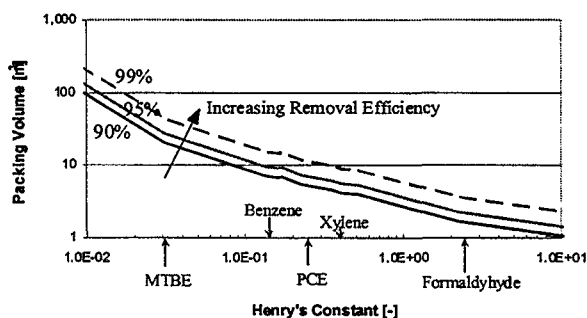
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Required Packing Volume for Several Chemicals

Required Packing Volume for Several Chemicals



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Treatment Costs for MTBE Removal From Groundwater

▲ Assumptions

- amortized capital, 20 yrs @ 4%
- 1997 prices for all equipment
- treatment to achieve >95% removal (700 ppb to 35 ppb)

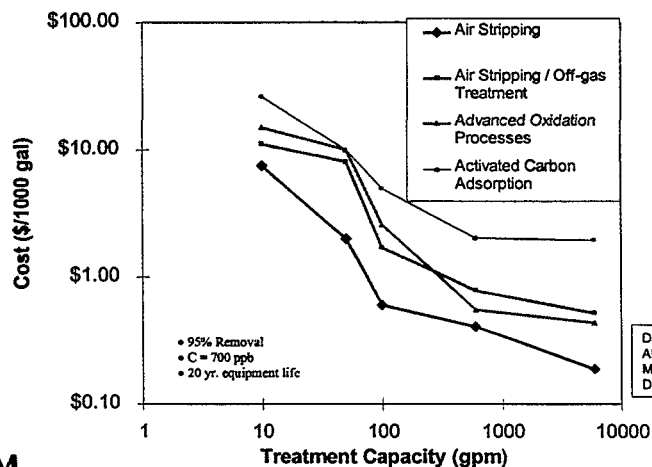
Technology	Annual Capital and O&M Cost (\$/1,000 gallons)	
	6,000 gpm	600 gpm
PTA	\$0.19	\$0.41
PTA / Thermal	\$0.52	\$0.78
UV / Peroxide	\$0.44	\$0.55
GAC	\$1.96	\$2.03

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Unit Costs for MTBE Treatment

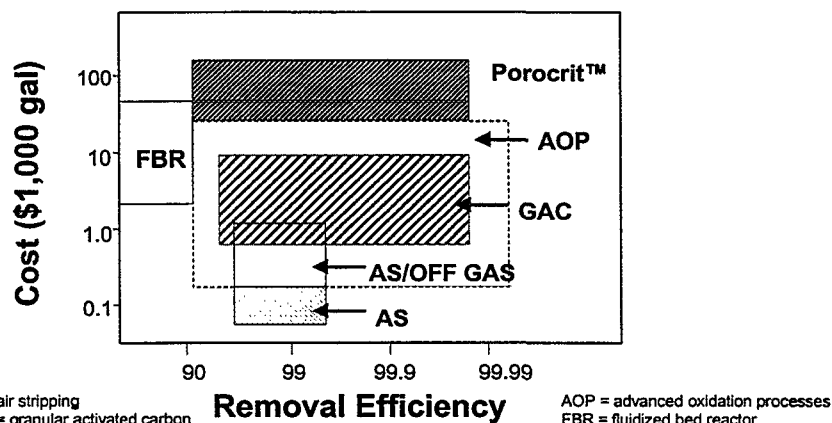


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MTBE Removal for Drinking Water Application



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Impact of Lower Target Treatment Goal on Costs for Water Treatment

- ▲ Unit costs site specific
- ▲ Major driver - treated water quality goal/standard

6,000 gpm System
Influent Concentration 700 ppb

Effluent Quality (ppb)	Technology	Unit Cost (\$/1,000 gal)
70	PTA, 1 column/thermal	0.50
35	PTA, 1 column/thermal	0.52
10	PTA, 1 column/thermal	0.55
<5	PTA, 2 columns/thermal on 1 column	0.67

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Cost Summaries -- In-Situ

Technology	\$ / cu. Yd.
▲ Soil Vapor Extraction	▲ \$30 - \$50
▲ Air Sparging/SVE	▲ \$50 - \$70
▲ Thermal Desorption	▲ \$100 - \$300
▲ ORC Oxidation	▲ ??

Unit Cost Highly Site Specific

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Technical Strategies: MTBE Refinery Spill

- ▲ Concentration Ranges - up to 40,000 ppm
- ▲ Treatment Target - 0.1 - 10 ppm
- ▲ Promising Options: Soil and Groundwater
 - SVE or dual phase
 - Biological system + air stripping
 - Steam stripping
 - Liquid/liquid extraction

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Technical Strategies: MTBE LUFT Source Area

- ▲ Concentration Ranges - 10 - 1,000 ppm
- ▲ Treatment Targets - groundwater: 0.005 - 1
- ▲ Promising Options: Groundwater: In-Situ
 - Pump and treat (AS/GAC/AOP)
 - Dewatering/SVE
 - Air stripping/SVE
 - Steam injection/recovery

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Technical Strategies: MTBE LUFT Distal Plume

- ▲ Concentration Ranges - .01 - 1 ppm
- ▲ Treatment Targets - groundwater: 0.005 ppm
- ▲ Promising Options: Groundwater
 - Pump and treat (AS/GAC/AOP)
 - Air sparging/SVE
 - In-situ oxidation
 - Barriers (e.g. ORC)
 - In-well aeration

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Technical Strategies: MTBE in Drinking Water - Low Bromide (<0.1 ppm)

- ▲ Concentration Ranges - .01 - 1 ppm
- ▲ Treatment Targets - SMCL: 0.005 ppm
- ▲ Promising Options:
 - AOP
 - AS with off-gas treatment

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Technical Strategies: MTBE in Drinking Water - High Bromide (>.1 ppm)

- ▲ Concentration Ranges - .01 - 1 ppm
- ▲ Treatment Targets - SMCL: 0.005 ppm
- ▲ Promising Options:
 - AOP w/o O₃
 - AOP w O₃ /bromate control
 - Packed tower with off-gas treatment
 - Surface aeration w/o off-gas

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MTBE Remediation and Treatment Alternatives Conclusions

- ▲ "Tool kit" for MTBE control extensive and growing
- ▲ Technology selection and costs are highly site specific - few simple cases
- ▲ Ex-situ options available commercially, several new options in development - need for credible, independent evaluations (e.g. certification)
- ▲ In-situ options face familiar constraints
 - site characterization limitations
 - slow rate of aerobic biodegradation
 - difficult in-situ mixing conditions
 - slow mass transfer
- ▲ The good news - low adsorption, LNAPL, volatile in neat form
- ▲ A manageable, not an intractable engineering challenge

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PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Overview of Perchlorate Issues

Lieutenant Colonel Dan Rogers

Background

Perchlorate anion (ClO_4^-) originates as a contaminant in the environment from the solid salts of ammonium, potassium, or sodium perchlorate. Perchlorate salts are quite soluble in water. The resultant anion (ClO_4^-) is exceedingly mobile in aqueous systems and can persist for many decades under typical groundwater and surface water conditions, due to kinetic barriers to its reactivity with other available constituents. Ammonium perchlorate is manufactured for use as an oxidizer component in solid propellant for rockets, missiles, and fireworks. Because of its shelf life, it must be periodically washed out of the country's missile and rocket inventory and replaced with a fresh supply. Thus, large volumes of the compound have been disposed of in Nevada, California, Utah, and likely other states, since the 1950's. Ammonium perchlorate is also used in certain munitions, fireworks, the manufacture of matches, and in analytical chemistry.

Potassium perchlorate had, until recently, been used therapeutically to treat hyperthyroidism resulting from an autoimmune condition known as Graves' disease. Potassium perchlorate is still used diagnostically to test thyroid hormone (TSH, T3 and T4) production in some clinical settings. The basis for the effect on thyroid hormone function is the competitive inhibition of iodide anion uptake by perchlorate which results in reduced thyroid hormone production. Thyroid hormone deficiencies can affect normal metabolism, growth and development. The limited database on the toxicology of perchlorate confirms its potential to disrupt thyroid hormone production in mammalian test species, but no robust data exist to evaluate the dose-response for this thyroid effect or to evaluate other potential target tissues or effects. There are no existing data to evaluate the effects of perchlorate in potentially susceptible population such as developing fetuses or to evaluate its effects on ecological systems. Studies are now underway to evaluate these potential effects.

Issues

Perchlorate is of concern because of the existing uncertainties in (1) the toxicological database documenting its health effects at low levels in drinking water; (2) the actual extent of the occurrence of perchlorate in ground and surface waters, which is compounded by some uncertainty in the validation of the analytical detection method; (3) the efficacy of different treatment technologies for various water uses such as drinking water or agricultural application; and (4) the extent and nature of ecological impact or transport and transformation phenomena in various environmental media.

This discussion paper was prepared for an Interagency Perchlorate Steering Committee stakeholders forum, May 19-21, 1998, and does not represent any of the participating agencies' policy.

This background discussion paper will provide you with general information and how plans are underway to integrate all the new information from a variety of areas in order to characterize the potential risk that perchlorate contamination may pose. Additional discussion papers will provide you with more in-depth information on these areas, including: (1) development of reliable analytical methods to detect perchlorate; (2) where perchlorate has been found; (3) the assessment of the health effects and toxicology studies to derive a benchmark value by which to evaluate risk; (4) research underway to evaluate the ecological impacts; and (5) development of treatment technologies to address various water uses.

Where Perchlorate Contamination Occurs

Within several months following the April 1997 development of a low level detection methodology, perchlorate had been discovered at various manufacturing sites and in well-water and the drinking water supplies in California, Nevada, and Utah. At this time, there has not been a systematic national survey of perchlorate occurrence. Only a relatively small number of water supplies have been monitored using the more sensitive method, primarily in the western states with a few sample results now available in the south.

The majority of locations where perchlorate has been detected in the groundwater are in California, associated with twelve facilities which have manufactured or tested solid rocket fuels for the Department of Defense (DoD) or the National Aeronautics and Space Administration (NASA). Two facilities which manufactured ammonium perchlorate in Nevada were found to have released perchlorate to groundwater which is the source for low levels (4 to 16 ppb) in Lake Mead and the Colorado River. This water is used for drinking water supply, irrigation and recreation for millions of people in Nevada, California, Arizona, and Native American Tribes. Other releases have been detected in Utah and Texas.

Information on other potential sites across the country is being gathered from DoD and NASA searches and from U.S. Environmental Protection Agency (EPA) information requests made to perchlorate manufacturers. Initial records indicate that perchlorate has been shipped to facilities in 37 states. EPA has notified State, Tribal, and local governments when it has evidence of perchlorate manufacture and use in their jurisdictions.

Interagency Perchlorate Steering Committee (IPSC)

An Interagency Perchlorate Steering Committee (IPSC) was formed in January 1998 to bring together government representatives from the EPA, DoD, Agency for Toxic Substances and Disease Registry (ATSDR), National Institute for Environmental Health Sciences (NIEHS), and affected State, Tribal, and local governments. Participation in the IPSC has also been solicited from other governmental entities.

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The charter of the IPSC is to facilitate and coordinate accurate accounts of related technological issues (occurrence, health effects, treatability and waste stream handling, analytical detection, and ecological impacts) and to create information transfer links for interagency and intergovernmental activities regarding these areas of concern.

The IPSC recently collaborated with EPA's Office of Research and Development (ORD) on a report to a Congressional House committee that assesses the state-of-the-science on the health effects of perchlorate on humans and the environment and the extent of perchlorate contamination. The report also contained recommendations for future research to address emerging issues.

Monthly teleconferences are held to update participants on events and breaking news regarding controversial or technological issues. Public meetings, such as the May 1998 meeting in Henderson, Nevada, will be held to distribute the most current scientific information on the key issues and to hear stakeholder and public concerns.

An Integrated Approach to Risk Characterization: Current Activities

A number of key pieces of information are necessary to characterize the risk of perchlorate contamination in order to formulate appropriate management strategies to mitigate potential risk. Accurate characterization of exposures rely on reliable analytical detection methods. The exposure estimates can not be gauged with respect to their risk unless a robust health risk estimate is available. Treatment technologies should be targeted to levels of concern and tailored to the intended use of the water. Research to obtain additional data and development of new methods or applications are underway in most of these areas to ensure that the state-of-the-science is brought to bear on addressing the unique issues of perchlorate contamination. Technology transfer is necessary so that all affected parties and concerned citizens are apprised of accurate and reliable information that is up to date with the evolving state-of-the-science.

Reliable Analytical Methods

As noted above, the first critical data needed for a comprehensive risk characterization is accurate information on occurrence: where the contamination occurs, the nature (type) and extent (magnitude) of the exposure. Occurrence survey studies require a reliable and accurate analytical method for detecting perchlorate in drinking water and various aquifer types or other environmental media (e.g., irrigated food crops). Ion chromatography (IC) is the state-of-the-art technology for analysis because historical methods based on gravimetry, spectrophotometry, or atomic absorption are non-specific for perchlorate. There are several existing IC methods, including the recent analytical method developed by the California Department of Health Services (CA DHS), Dionex, and one developed by the Air Force Research Laboratory/Operational Toxicology Branch (AFRL/HST). These methods depend upon

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retention time in a standard to identify any peak with the same or similar retention time as perchlorate in a water sample. The robustness of existing IC methods for the analysis of perchlorate in water with high total dissolved solids has been questioned. Research is underway that will evaluate the variability, reproducibility, accuracy and precision of the IC methods across laboratories and to determine the appropriate concentration ranges for measurement.

Health Effects Assessment

The second critical piece of information is to have a comprehensive health effects evaluation that can serve as the basis for development of exposure guidance levels. The toxicology data available to evaluate the potential health effects of perchlorate are extremely limited. The EPA Superfund Technical Support Center issued a provisional reference dose (RfD) in 1992 and a revised provisional RfD in 1995. The provisional RfD values (1992 and 1995) were based on an acute study in which single doses of potassium perchlorate caused the release of iodide from the thyroids of patients with Graves' Disease. Uncertainty factors that ranged from 300 to 1000 were applied to account for missing endpoints and extrapolations required to calculate a lifetime human exposure level. Standard assumptions for ingestion rate and body weight were then applied to the RfD to calculate the reported range in the ground water cleanup guidance levels of 4 -18 parts per billion (ppb). The CA DHS adopted 18 ppb as its provisional action level. An RfD is calculated as an estimate of a daily human exposure that will result in no deleterious noncancer effects over a lifetime. Ideally, an RfD is based on a database that evaluates an array of endpoints that address potential toxicity during various critical lifestages, from developing fetus through adult and reproductive stages. New studies were begun in 1997 and are underway to provide data on these missing endpoints. Additional new studies will also provide data to evaluate the potential for cancer risk. The National Center for Environmental Assessment (NCEA) in the Office of Research and Development (ORD) of the EPA plans to evaluate these new data and issue a new assessment with a revised RfD at the end of September 1998. The new assessment, all the new data and the study protocols will then be subjected to an external peer review in October 1998 before the assessment is finalized.

Ecological Impact Assessment / Transport and Transformation

Another potential area of health impact is on ecosystems and via indirect exposure pathways (e.g., agriculture or fishing). Searches of available databases have revealed minimal information on the ecological effects of ammonium perchlorate or any of its other salts. Essentially no reliable data exist for its effects on various soil, sediment or aquatic receptors including: aquatic vertebrates, aquatic or sediment invertebrates, bacteria or plants. Approaches for the evaluation of effects on ecological receptors is complicated by the lack of data on its environmental transport and transformation processes. These include data on the effects of soil chemistry (soil composition, adsorption processes, particle size and water saturation, complexation behavior with humic and fulvic materials, pH, etc.), movement characteristics in various media, adsorption to soils of high and low cation and anion exchange capacity, and the effect of ammonia. Development of predictive environmental transport and transformation

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models would be useful both to assessing ecological impact as well as directing sampling strategies to determine occurrence monitoring sites. Research has been recommended to develop data on the effects of perchlorate on various ecological receptors and the various parameters needed to develop reliable transport and transportation models that can forecast the fate of perchlorate in various aquifer types and environmental media.

Treatment Technologies

The health estimate such as the oral RfD is typically compared against the exposure estimates to characterize potential health risks. Such a comparison will also target the levels to which reliable treatment technologies must be developed. Perchlorate is very unreactive towards most reducing agents when cold and dilute and has low reactivity as an oxidant due to kinetic barriers. These same properties make developing treatment technologies difficult, especially at low concentration levels. No one technology or process will likely provide an effective solution for every occurrence of perchlorate contamination in water supplies due to a large number of independent variables. Different technology may also be developed depending upon the intended use of the treated water (e.g., drinking water versus agricultural application). Treatment technologies and processes have been developed by industry and the Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/MLQE) to recover perchlorate for reuse and to treat residual wastewater containing high concentrations of perchlorate, i.e. 500-10,000 parts per million (ppm), from the manufacture and maintenance of rocket motors. Research is underway to develop technologies that meet the new challenge of treating low-concentration (5 ppb to 500 ppm) perchlorate contamination present in ground and surface water supplies.

EPA's Future Regulatory Plans:

The Safe Drinking Water Act (SDWA), enacted by Congress in 1974 and amended in 1986 and 1996, provides the basis for safeguarding public drinking water systems from contaminants that pose a threat to public health. The purpose of SDWA is to protect public health by ensuring that public drinking water systems provided tap water that is safe for drinking and bathing. Within EPA, the Office of Ground Water and Drinking Water (OGWDW) develops National Primary Drinking Water Regulations (NPDWR) to control the levels contaminants that may occur in public drinking water systems.

The 1996 amendments to the SDWA require EPA to publish a list of contaminants that are not currently subject to a NPDWR and are known or anticipated to occur in public water systems. This list, known as the Contaminant Candidate List (CCL), will be the source of priority contaminants for research, guidance development, and selection of contaminants for making regulatory determinations and/or monitoring by the States. The SDWA requires EPA to make a determination of whether or not to regulate not less than 5 contaminants from the CCL by 2001. The CCL must also be reviewed and updated every 5 years, or again in 2003.

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With broad public input and consultation with the scientific community, a draft CCL was published on October 6, 1997. The draft CCL specifically requested comment on whether to include perchlorate on the CCL based on the limited information EPA had received on its occurrence in drinking water supplies at the time of publication. As a result of the public comments and additional occurrence information obtained, the Agency determined that sufficient information exists to raise concern over perchlorate's potential public health impact, and it was added to the final CCL published on March 2, 1998.

The CCL consists of 50 chemical and 10 microbiological contaminants and is divided into two categories: (1) contaminants for which sufficient information exists to begin to make regulatory determinations by 2001, and (2) contaminants for which additional research and occurrence information is necessary before regulatory determinations can be made. Perchlorate is identified as a contaminant needing additional research in the areas of health effects, treatment technologies, analytical methods, and more complete occurrence data.

State Regulatory Plans:

In 1997, the CA DHS and California EPA's Office of Environmental Health Hazard Assessment reviewed the EPA risk assessment reports for perchlorate. As a result, California established its action level of 18 ppb. Perchlorate concentrations lower than 18 ppb are not considered to pose a health concern for the public, including children and pregnant women. CA DHS advises water utilities to remove drinking water supplies from service if they exceed the 18 ppb action level. If the contaminated source is not removed from service due to system demands and if drinking water that is provided by the utility exceeds the action level, CA DHS will advise the utility to arrange for public notification to its customers. On August 1, 1997, CA DHS informed drinking water utilities of its intention to develop a regulation to require monitoring for perchlorate as an unregulated chemical. Legislative action to establish a state drinking water standard for perchlorate has been introduced but has not been brought to a vote (CA Senate Bill 1033).

The Nevada Division of Environmental Protection (NDEP) has authority under Nevada Water Pollution Control Regulations to address pollutants in soil or groundwater that pose a threat to the waters of the state. The State's Corrective Action Regulations direct NDEP to establish Action Levels for hazardous substances, pollutants or contaminants using drinking water standards (MCLs), background levels or protective levels (determined by IRIS or equivalent). In August, 1997, Nevada determined that the health-based action level of 18 ppb, as established in California, would be the recommended action level for cleanup pending a more current risk assessment.

No other state is known to have adopted action levels for perchlorate primarily since levels greater than 18 ppb have not been found in water supplies in other States.

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Technology Transfer and Public Outreach

Accurate information and communication tools are needed to keep the general public, water utilities and their customers informed regarding the state-of-the-science and important issues related to perchlorate toxicity, including: analytical detection methods, occurrence, treatment technologies, ecological impact, and environmental transfer and transformation.

Bringing effective water treatment technologies to bear on perchlorate contaminated drinking water quickly and affordably is one of the primary goals of technology transfer. This requires emphasis on two important factors in the rapid development and implementation of new technologies. First, information regarding technology development and application activities should be disseminated to the widest possible audience. The IPSC will continue to collect and disseminate information regarding treatment technologies and remain involved in facilitating research and technology demonstration efforts. Effective tools that reach a broad spectrum of the public, such as discussion papers, teleconferences, an updated Web page, and news releases have been developed. Subcommittees of the IPSC are been charged with developing and updating discussion papers. EPA's Office of Water (OW) is developing a website with links to the Office of Solid Waste and Emergency Response (OSWER) and the National Center for Environmental Assessment (NCEA). EPA regional offices have been working with State authorities on news releases.

Second, drinking water authorities and purveyors of drinking water treatment technologies need to be involved as partners in research and technology demonstration. The IPSC will again serve to coordinate these activities as required. Attention to these key technology transfer issues will ensure that sound treatment strategies are developed and implemented which are responsive to the unique requirements of each affected area.

PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Health Effects / Toxicology of Perchlorate

Introduction

A significant portion of the expedited research underway to address perchlorate contamination in the environment has been dedicated to obtaining a reliable and comprehensive data base on the health effects and toxicology of perchlorate. Such robust data are necessary to develop a health risk assessment that includes an estimate called a reference dose (RfD) which can be used to evaluate the potential risk of human exposures. The RfD can also be used in risk management programs to help guide the range where analytical methods must be effective and to target treatment technologies. The health effects data serve as the lynchpin in the overall integrated approach to addressing the emerging issues of perchlorate contamination.

Background

The currently available database on the health effects and toxicology of perchlorate or its salts is very limited. The majority of human data are clinical reports of patients treated with potassium perchlorate for hyperthyroidism resulting from an autoimmune condition known as Graves' disease. Potassium perchlorate is still used diagnostically to test thyroid hormone [thyroid stimulating hormone (TSH), triiodothyronine (T3), and thyroxine (T4)] production in some clinical settings. The basis for the effect on thyroid hormone function is the competitive inhibition of iodide anion uptake into the thyroid gland by perchlorate anion (ClO_4^-) which then results in reduced thyroid hormone production.

It is difficult to establish a dose-response for the effects on thyroid function from daily or repeated exposures in normal humans from the data on patients with Graves' disease because of a variety of confounding factors, including: the effect of the disease, that often only a single exposure and not repeated exposures were tested, that only one or two doses were employed, and that often the only effect monitored was iodine release from the thyroid or control of the hyperthyroid state. There are limited data in normal human subjects and laboratory animals that support the effect of perchlorate on thyroid hormones, but the majority of these additional studies suffer from the same limitations with respect to the number of doses and exposures. These limitations prevent establishment of a quantitative dose-response estimate for the effects on thyroid hormones after long-term repeated exposures to perchlorate in healthy human subjects. The typical objective of a health risk assessment is to evaluate a comprehensive array of testing endpoints that represent various life stages in which potential effects could occur, e.g., the developing fetus through adult and for effects on reproductive capability. Thyroid hormone deficiencies, such as those induced by perchlorate, can affect normal metabolism, growth and development. No robust data exist to evaluate other potential target tissues or effects. There are no data to evaluate the effects of perchlorate in potentially susceptible population such as developing fetuses, nor are there data on the effects of perchlorate on reproductive capacity of male or female laboratory animals.

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Benign tumors have been reported in the thyroids of male Wistar rats and female BALB/c mice treated with repeated, high dose exposures (2 years at 1,339 and 46 weeks at 2,147 mg/Kg-day, respectively) of potassium perchlorate in drinking water. Benign tumors in the thyroid have been established to be the result of a series of progressive changes that occur in the thyroid in response to interference with thyroid-pituitary homeostasis (i.e., perturbation of the normal stable state of the hormones and functions shared between these two related glands). This progression is similar regardless of the cause of the thyroid hormone interference (Hill et al., 1989; Capen, 1997; Hurley et al., submitted). The EPA has adopted the policy that an assumption of a threshold based on these precursor lesions along the progression is appropriate for the dose-response of chemicals which cause this type of disruption in the thyroid when they do not have genotoxic activity, i.e., cause damage to DNA or show other genetic disruption (U.S. EPA, 1998). Therefore, a dose-response estimate established using the no-observed-adverse-effect level for the precursor lesions should be an estimate also protective for potential benign tumor development. Existing shorter-term studies indicate that perchlorate causes changes in the thyroid typical of the progression described and genotoxic studies are underway to establish that perchlorate does not have any activity relevant to carcinogenicity.

Provisional Health Risk Assessment

The EPA Superfund Technical Support Center issued a provisional reference dose (RfD) in 1992 and a revised provisional RfD in 1995. An RfD is calculated as an estimate of a daily oral human exposure that will result in no deleterious noncancer effects over a lifetime. Ideally, an RfD is based on a database that evaluates an array of endpoints that address potential toxicity during various critical lifestages, from developing fetus through adult and reproductive stages. The provisional RfD values (1992 and 1995) were based on an acute study in which single doses of potassium perchlorate caused the release of iodide from the thyroids of patients with Graves' Disease. The no-observed-adverse-effect-level (NOAEL) was determined to be 0.14 mg/Kg-day based on release of iodine in the thyroid followed by incomplete inhibition of iodine uptake. Uncertainty factors that ranged from 300 to 1000 were applied to account for data missing on additional endpoints and extrapolations required to calculate a lifetime human exposure level. Standard assumptions for ingestion rate and body weight were then applied to the RfD to calculate the reported range in the ground water cleanup guidance levels of 4 -18 parts per billion (ppb). The California Department of Health Services (CA DHS) adopted 18 ppb as its provisional action level.

The provisional RfD values issued are listed by the EPA only as provisional because they did not undergo the internal Agency and external peer review required of estimates available on the EPA's Integrated Risk Information System (IRIS). The outcome of an external peer review convened in March 1997 of an analogous RfD derivation by an independent organization, Toxicology Excellence for Risk Assessment (TERA), was the determination that the health effects and toxicity data were insufficient for a credible quantitative risk analysis. The external peer review panel concluded that the data were not sufficient to rule out effects of perchlorate on other organs, so that it could not be determined unequivocally that the effects on the thyroid were the critical effect. In particular, the reviewers were concerned that developmental toxicity, notably neurological development due to hypothyroidism during pregnancy, could be a critical effect of perchlorate that has not been adequately examined in studies to date.

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New Health Effects / Toxicology Studies Underway

In response to the March 1997 external peer review of the provisional RfD value, a subsequent external peer review of experts was convened in May 1997 to recommend and prioritize a set of studies to address the key data gaps and reduce uncertainties in various extrapolations. The objective of the new studies is to provide a comprehensive database that provides for development of a robust RfD estimate that reduces the uncertainties inherent in the provisional values. Funding for the studies was procured and obligated through a variety of sources, principally the USAF and the Perchlorate Study Group (PSG).¹ The protocols for the studies were reviewed by external peer reviewers from the EPA, California EPA, academia, industry, private institutes and Health Canada. The timeframe for the development of these new data has been precedent setting and has been a direct result of a unique partnering initiative. Typical research and development mechanisms would have required a number of years to accomplish these same studies.

Eight new studies were recommended in order to provide a comprehensive array of endpoints. These are described below along with their anticipated role in informing the revised health risk assessment.

(1) 90-Day Subchronic Oral Bioassay Study. This study is considered the minimum data requirement for derivation of an oral RfD. The study will identify other target tissues, test young adult rats, and also provide data on the effect of repeated exposure to perchlorate on thyroid hormone levels. These data may also allow reduction of the uncertainty factor applied for database deficiencies.

(2) Neurobehavioral Developmental Study. This study will evaluate the potential for developmental neurotoxicity of perchlorate by assessing functional and morphological endpoints in offspring from mother exposed during pregnancy and lactation. Neurotoxicity endpoints may be a critical effect and the developing organism a sensitive subpopulation. These data may allow reduction of the uncertainty factors applied for intrahuman variability and database deficiencies.

(3) Segment II Developmental Study. This study will evaluate the potential for perchlorate to cause birth defects in rabbits and will identify a potentially critical effect and subpopulation. This study will also provide data on the thyroid hormone effects in a second species (in addition to rats). These data may allow reduction of the uncertainty factor applied for database deficiencies.

¹The PSG is a consortium of defense contractors and manufacturers including: Alliant Techsystems, American Pacific/Western Electrochemical Company, Atlantic Research Corporation, Lockheed Martin, Thiokol Propulsion Group, and United Technologies Chemical Systems.

(4) Two-Generation Reproductive Toxicity Study. This study will evaluate the potential for perchlorate to cause deficits in reproductive performance in adult rats and for toxicity in the young offspring. This study may identify a potentially critical effect and allow for reduction of the uncertainty factor applied for database deficiencies.

(5) ADME (Absorption, Distribution, Metabolism, and Elimination) Studies. These studies will be performed to understand the pharmacokinetics (how perchlorate is absorbed, distributed, metabolized and excreted) of perchlorate in test animals and humans. These data will provide information that will allow construction of quantitative extrapolation of dose across species (e.g., rat to human).

(6) Perchlorate Mechanism Studies. These studies will be conducted by a comparison of the existing literature and of new *in vitro* and *in vivo* data that evaluate the effects of perchlorate on the iodide uptake mechanism across species to aid in the quantitative extrapolation of dose.

(7) Genotoxicity Assays. These studies will evaluate the potential for carcinogenicity by evaluating mutations and toxic effects on DNA. These data will be useful to evaluate whether the benign thyroid tumors are likely to be a result of the proposed threshold pathogenesis process.

(8) Immunotoxicity Studies. These studies will evaluate the potential for perchlorate to disrupt immune function and identify a potentially critical effect. These data may help to reduce the uncertainty factor applied for database deficiencies.

Additional work may be required to mathematically model the dosimetry (pharmacokinetics) and toxic effects in order to increase the accuracy of a health risk determination, but this will need to be evaluated as the new data become available. An epidemiological study has been proposed to look at infant thyroid hormone data from mothers who were exposed in their drinking water supplies. The analysis would rely on the dose reconstruction data to the level of either a city or census block and will assume either that all women who lived in that area were exposed to that level of perchlorate or impose standard assumptions from other such studies (e.g., 20% of women drink bottled water). The dose reconstruction of what was in the water would have to be constructed on occurrence data once the hydrology in the aquifers and transport and transformation processes can be worked out. Both of these studies are considered refinements to the revision of the RfD that will likely result from the new studies.

EPA Plans for Revised Health Assessment and Peer Review

Revised Health Risk Assessment

The National Center for Environmental Assessment (NCEA) in the Office of Research and Development (ORD) of the EPA plans to evaluate the health effects and toxicology data from these new studies and then issue a new assessment at the end of September 1998. The new assessment, all the new data, and the study protocols will then be subjected to an external peer review in October 1998 before the assessment is finalized. The assessment, data, and protocols will be available to the public at the time of release to external peer review.

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Once finalized, this new peer-reviewed health assessment and new oral RfD will serve as a more robust health effects estimate than the existing provisional values with which to evaluate exposure estimates in order to characterize potential risk from perchlorate contamination or with which to develop guidance levels for cleanup and to target treatment technologies.

External Peer Review of Revised Assessment

Independent, external peer review of the study protocols, toxicity studies, and revised reference dose and health assessment for perchlorate will be critical to ensuring that future decisions based on the RfD will be protective of human health. EPA's Office of Solid Waste and Emergency Response (OSWER) will task a qualified contractor to manage peer review of technical issues related to the development of the reference dose, including study design, conduct of toxicity studies, statistical treatment of data, selection of critical effect, selection of uncertainty factors and risk characterization. The peer review will be conducted by a panel of technical experts in developmental toxicology, reproductive toxicology, genetic toxicology, general toxicology, pathology, biostatistics, dose-response modeling and risk assessment. Peer reviewers will be selected from a pool of candidates nominated by stakeholders in the perchlorate issues. The RfD assessment package, supporting studies, and study protocols for the new data will be distributed to the peer review panel in advance of the peer review meeting. Peer reviewers will independently review the RfD assessment package and supporting studies, and will submit their written comments to OSWER's contractor prior to the peer review meeting. The peer reviewer's comments will be compiled by OSWER's contractor and will be distributed to all of the peer reviewers and the public in advance of the meeting. The peer reviewers will gather for a two day meeting in a location selected based on accessibility to stakeholders and the peer reviewers. The public will be invited to attend and observe the peer review meeting. Following the peer review meeting, the peer review panel will generate a report detailing their comments on the reference dose package and supporting studies. EPA NCEA will generate a responsiveness summary report which will discuss in detail how they will address the comments raised by the peer reviewers. The provisional reference dose will subsequently be issued by EPA.

Questions for Discussion

1. What are the effects of hypothyroidism in adults versus infants?
2. What relevance do these effects have to children's health?
3. What are the potential impacts to pregnant women who drink contaminated water?
4. How will new information on health effects be used in the future?

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PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Ecological Effects/Transport and Transformation

Background

Perchlorate salts are quite soluble in water. The resultant anion (ClO_4^-) is exceedingly mobile in aqueous systems and can persist for many decades under typical groundwater and surface water conditions, due to kinetic barriers to its reactivity with other available constituents. This mobility and persistence may pose a threat to ecological receptors and whole ecosystems, either by direct harm to organisms, or it may indirectly affect their ability to survive and reproduce.

Currently, there are no data to evaluate the effects of perchlorate on ecological systems nor is there data about the possible uptake of perchlorate into agricultural products through irrigation of the food crops. Analytical tests have been derived to detect perchlorate in water, but little is known about testing food crops for perchlorate.

This fact sheet will describe historical studies of perchlorate on non-human receptors. Next, it will present tests proposed by the U.S. Environmental Protection Agency (EPA) and the U.S. Air Force (USAF) to address the current gaps in knowledge. The information gained from these screening-level tests will be used to support recommendations for further studies. Lastly, this fact sheet will outline the effort by the USAF to determine fate and transport of ammonium perchlorate in the environment.

Historical Studies

Searches of available databases have revealed minimal information on the ecological effects of ammonium perchlorate or any of its other salts. Little data exist to describe its effects on various soil, sediment or aquatic receptors including: aquatic vertebrates, aquatic or sediment invertebrates, bacteria or plants. The data that is available suggest effects on thyroid-hormone mediated development in the South African clawed frog, *Xenopus laevis* in the range of 50-100 parts per million (ppm); and 1000 ppm in recent studies has been shown to completely block the metamorphosis of tadpoles. Effects on development and population growth have also been indicated in the freshwater sea lamprey at 100 ppm and the freshwater hydra at 350 ppm. Mortality was observed in cold water trout (6000-7000 ppm) and *Daphnia magna* (670 ppm). Effects on seed germination and growth of agricultural plants were reported at 10 ppm.

Proposed Activities

The USAF/Detachment 1, Human Systems Center, Brooks AFB, in conjunction with EPA, has developed a proposal for a battery of screening level bioassays in laboratory-reared organisms

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representative of ecological receptors across soil, sediment, and water column receptors to evaluate dose-response relationships. The identified tests focus on identifying gross (direct) toxicity tests whose endpoints can include mortality, growth, and reproductive success. Dose response relationships can be evaluated.

In general, the tools used to evaluate chemical effects on soil and benthic invertebrates, plants, and fish include benchmark values, toxicity tests, bioaccumulation estimates, and field studies. In the absence of accepted benchmark values, a tiered approach to a toxicity assessment of effects on ecological receptors is suggested. The purpose of a tiered approach is to do necessary and sufficient amount of work to characterize risk to an ecological receptor with an acceptable degree of uncertainty. In this approach to describe ecological impact of perchlorate, Tier 1 included the literature search described under Historical Studies. Tier 2 will include the tests shown below. If significant toxicity is demonstrated in a suite of bioassays more sophisticated assessments can be implemented. Bioassays with standard protocols and general regulatory acceptance were chosen.

Proposed tests include:

Test Organism	Matrix
<i>Daphnia magna</i> or <i>Ceriodaphnia dubia</i>	Sediment invertebrate
<i>Chironomus tentans</i>	Larval sediment invertebrate
<i>Hyallela azteca</i>	Sediment invertebrate
<i>Lemna minor</i> (duckweed)	Vascular plant (aquatic)
Fathead minnow	Aquatic vertebrate
Earthworm	Soil invertebrate
Microtox	bacteria (marine)

Although these are screening level tests and only give us an idea of gross toxicity, they will provide needed dose-response information to make decisions on the need for the next tier of tests (Tier 3) to be completed as required (e.g., bioavailability, bioaccumulation, histopathology, etc.).

Transport and Transformation:

The USAF has begun to determine the transport and transformation (also called fate and transport) of ammonium perchlorate in the environment. This information can be used to predict the flow of perchlorate in the subsurface. Currently, a literature search has been completed which describes fate and transport of ammonium perchlorate in the subsurface. The study identifies and assesses factors such as solubility, adsorption, biodegradation, chemical reactions, dispersion, diffusion, and other processes affecting fate and transport of perchlorate.

The literature shows perchlorate to be non-volatile, so inhalation of perchlorate vapor is not expected. However, perchlorate salts do exhibit high solubility in water, which leads to high mobility in surface water and groundwater. Its density is nearly twice that of water, so it will sink in water. Concentrated solutions are also more dense than water. Because perchlorate salts are so

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soluble, perchlorate ion will predominate in solution. However, potassium is less soluble than ammonium, so it is possible that potassium perchlorate may precipitate ("salt-out") of solution, decreasing migration.

Perchlorate is a kinetically stable ion, which means that reduction of the chlorine atom from a +7 oxidation state in perchlorate to a -1 oxidation state as a chloride ion does not occur spontaneously—it would require a input of energy (e.g., heat or light) or the presence of a catalyst to help the reaction occur.

Dilution and precipitation reactions are presumed to have the most significant effect on perchlorate migration. Through dilution, concentrations would be expected to be significantly less away from the source. Precipitation, can help decrease mobility of perchlorate, but the salt can then re-dissolve, be transported, and precipitate repeatedly. Sorption is not expected to attenuate perchlorate since it absorbs weakly to most soil minerals. Since perchlorate is chemically stable, natural chemical reduction in the environment is not expected to be significant.

The treatment technology subcommittee of the Interagency Perchlorate Steering Committee (IPSC) is examining biological reduction of perchlorate.

Based on the information gathered in this literature review, recommendations have been made for a second phase to fill many of the gaps in the current understanding of perchlorate transport and transformation. This will help develop models to predict and describe perchlorate migration in the subsurface.

Questions for Discussion

1. Do plants uptake the perchlorate ion when irrigated with perchlorate-containing water?
2. What tests can be used to determine if perchlorate is in the food crop?
3. Are there other ecological species that should be considered for potential effects from perchlorate?

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PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Analytical Methods

Introduction

In January of 1997, the California Department of Health Services' Division of Drinking Water and Environmental Management requested the Sanitation and Radiation Laboratory Branch (SRLB) to test for perchlorate in drinking water wells potentially affected by groundwater migrating from the Aerojet facility near Sacramento. Existing U.S. Environmental Protection Agency (EPA) risk assessment studies on perchlorate indicated that a reporting limit of at least 4 parts per billion (ppb) would be necessary. No procedures were available for measuring perchlorate at such low levels. An Ion Chromatographic (IC) method was capable of detecting 400 ppb and during the previous year Aerojet had improved the method to detect 100 ppb. By March 1997, SRLB and an analytical equipment manufacturer had developed an IC method that achieved a method detection limit of approximately 1 ppb and a reporting limit of 4 ppb. This method was used to detect perchlorate above the 4 ppb reporting limit in wells near the Aerojet site. Testing began on other wells throughout California, adjacent to sites that had known association with the use or manufacture of perchlorate-containing products. By January 1998, perchlorate had been detected in over 100 water supply wells in California and in Lake Mead and the Colorado River.

An increasing number of commercial and government laboratories have adopted the improved analytical method, leading to further discoveries of perchlorate contamination and an increase in monitoring water supplies. Development of a formal published method documenting the reproducibility and limitations of the technique is expected to facilitate the acceptance of perchlorate testing at low concentrations by laboratories across the country. The need for a reporting limit of 4 ppb taxes the sensitivity and reproducibility of the current IC method. A collaborative study of existing IC methods is planned for the near future. Work is also being planned to develop different analytical techniques to confirm the results of the IC method.

Monitoring water supplies and identifying possible sources of perchlorate contamination are not the only needs for analytical capability. A reliable and accurate method for analysis of perchlorate is essential for research in human health risk assessment, treatment technologies, and ecological toxicology. Results of these assessments may place additional requirements on analytical methods.

Characteristics of the Current Method

There are two components to perchlorate analysis, (1) separation of perchlorate from all other species in water, and (2) measurement of the separated perchlorate against suitable standards.

Separation

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Separation of perchlorate and other like dissolved species (anions) in water is based on the attraction (affinity) of perchlorate for a special organic exchanger (ion exchange resin) packed into a column for convenient use. The anions are carried through the column by a flow of solution (mobile phase or eluent). As the anions move through the column they separate into thin bands. Since the relative strength of the attraction of the different anions to the ion exchange resin is expected to be different for each dissolved specie, they separate and come off (elute from) the ion exchange column at different times. As the anions pass through the detector, the detector response is registered as peaks with a peak area or peak height proportional to concentration and at a retention time characteristic of the anion.

Detection

The separated bands of anions are detected by the electrical properties created by the combination of the mobile phase and anion in the detector at a given time. The property of the solution to conduct electrical charge is called the conductivity. A conductivity detector is able to detect and measure the subtle differences of solution conductivity and thereby measure the relative contribution of the anion of interest to the total conductivity.

Ideally, only the anion of interest would be present in the small volume of eluent containing the separated band of perchlorate while the eluent would be nonconducting, presenting the lowest background and highest sensitivity. Because the mobile phase is also conducting and adds to the overall background, the ideal situation can not be realized but something very close can be achieved. By removing (suppressing) the species in the mobile phase that contribute to the background but retaining the anion of interest by use of a special technique, conductivity, detection (sensitivity), and signal measurement can approach the ideal. This is the general approach used by most of the current IC methods.

Method Variations

Since the presence of perchlorate in various water supplies has become important, a number of method changes have been tried to increase the sensitivity of the IC method. The basic system components remain the same, an ion exchange column, eluent, some method of suppression, and conductivity detection. The hardware (pumps, tubing, materials of construction, the suppressor, and the detector) does not contribute directly to the chemistry of the separation. The chemistry of the eluent and the ion exchange resin seem the most promising variables to investigate at this time. Many laboratories and some commercial IC manufactures are presently engaged in this research and development.

Interferences

The elution time is the only parameter, at this time, that is used to determine if the peak can be presumed to be perchlorate. If other, yet unknown anions are also eluted at the same time as perchlorate, the IC method can not indicate the difference. If such were the case, the presence of

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and concentration of perchlorate would be unclear and a false positive would result with no method to further separate perchlorate from the interfering species. The common approach is to measure the elution times for other anions that might be present in water, alone and as mixtures with perchlorate. By a process of elimination it may be found that under a specified set of conditions perchlorate and only perchlorate will elute from the column. An attractive alternative is to develop a perchlorate-specific method which alone or in combination with IC would measure the concentration of perchlorate uninfluenced by any other chemical specie. This latter approach is a fertile, yet unexplored field of research and development.

Ongoing Actions and Next Steps

The analytical subcommittee of the Interagency Perchlorate Steering Committee (IPSC) is coordinating a collaborative study of the existing IC method and its variations. This method has been used to measure perchlorate in all water supplies where perchlorate has been tentatively identified. The subcommittee is composed of four scientists from EPA, the states of California and Utah, and the United States Air Force.

The referee facility is the EPA Office of Research and Development, Environmental Sciences Division, Environmental Chemistry Branch located in Las Vegas. The study design will evaluate the within laboratory precision (repeatability), between laboratory precision (reproducibility), method accuracy (bias), detection limit, and sensitivity. These are basic questions requiring an empirical (factual) solution. The results of this collaborative study will serve as a basis to focus future research and method development, with the overall goal to publish a standardized method or methods for low level perchlorate determination.

Questions for Discussion

Because the measurement of perchlorate will likely encompass other analytical strategies, the analytical subcommittee is interested in public comments on the following issue areas:

1. What are other IC technologies, if any? High pressure liquid chromatography, other anion exchanger not based on organic supports or modified surfaces?
2. What are other non IC technologies? Ion specific electrode, spectrophotometric methods, derivatization of perchlorate to facilitate detection by other techniques?
3. What are some possible analyte, perchlorate, specific method possibilities?
4. How do anions, such as chloride, fluoride, sulfate, sulfite, nitrate and nitrite, etc. and cations, such as sodium, potassium, and calcium commonly found in groundwater sources affect the ion chromatography, sensitivity, and specificity of perchlorate analysis?
5. Does the presence of organic solvent affect the ion chromatography, sensitivity and specificity of perchlorate analysis?
6. How stable is perchlorate in general, and with respect to light/dark storage conditions, container type, and the presence of other anions?

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PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Treatment Technologies

Introduction

Treatment technologies capable of removing perchlorate from water are urgently needed. Water utilities, in particular, need treatment methods that can reliably reduce perchlorate concentrations to low or non-detectable levels. Because the perchlorate ion is nonvolatile and highly soluble in water, it cannot be removed from water by conventional filtration, sedimentation, or air stripping. It appears to be only weakly removed by activated carbon. To be useful, a treatment method must be cost-effective, acceptable to regulatory agencies and the public, cause no other water quality problems, and minimize waste generation. The only option available for reducing perchlorate levels in contaminated water supplies is by blending uncontaminated supplies with those that containing perchlorate. In addition, the degree to which treatment options need to be developed is a function of the forthcoming results of the toxicology and health affects data and resulting peer reviewed reference dose for drinking water.

A few promising technologies are being developed for removal of perchlorate. Some are commonly used in water treatment, others less so. An anaerobic biochemical process has received the most attention, but reverse osmosis and ion exchange are also capable of removing perchlorate. Studies are underway to evaluate the cost, effectiveness, and implementability of these technologies.

The remainder of this fact sheet discusses the current state of perchlorate treatment technology, and current and planned treatment development efforts being carried out as part of U.S. Environmental Protection Agency (EPA) Superfund program studies, U.S. Air Force (USAF) research, water utility funded studies, and the federally funded research effort underway by the East Valley Water District, CA and the American Water Works Association Research Foundation (AWWARF). Technologies are grouped into three categories: physical, chemical, and biochemical.

Physical Processes (Ion Exchange, Reverse Osmosis, Nanofiltration)

There is no doubt that physical processes such as ion exchange and reverse osmosis can remove perchlorate from water. Of the two processes, ion exchange, in which the perchlorate ion is replaced by an innocuous anion (e.g., chloride), is currently receiving the most attention. Ion exchange technologies have not yet been used to remove low levels of perchlorate from drinking

This discussion paper was prepared for an Interagency Perchlorate Steering Committee stakeholders forum, May 19-21, 1998, and does not represent any of the participating agencies' policy.

water supplies, but have been widely used in drinking water treatment to remove higher concentrations of nitrate, an anion similar to perchlorate. Perchlorate and nitrate are weakly hydrated in solution, and similar technologies are expected to be applicable to the treatment of both ions. In California's San Gabriel Valley, the Main San Gabriel Basin Watermaster is the primary sponsor of bench and pilot-scale tests of the performance of ion exchange technologies, with results expected by mid-1998. The San Gabriel Valley study is evaluating the cost and effectiveness of removing approximately 30 to 200 parts per billion (ppb) perchlorate from groundwater.

One current challenge is to find an ion exchange resin that can selectively remove perchlorate, thereby limiting the unnecessary removal of other ions which are typically present in far higher concentrations than perchlorate (e.g., chloride, sulfate, bicarbonate). Ion exchange processes (and reverse osmosis and nanofiltration) also generate perchlorate-rich waste brines that may be difficult to dispose. Further treatment of the brine may be needed to reduce its volume or toxicity before disposal.

Nanofiltration and reverse osmosis will also remove perchlorate, but at unknown cost. Pilot-scale tests completed by Harvey Mudd College for the Metropolitan Water District of Southern California have shown that nanofiltration can reduce perchlorate from 18 ppb to less than 4 ppb in a contaminated surface water supply, but at undetermined cost. In addition, the Southern Nevada Water Authority reportedly achieved satisfactory results in tests of in-home reverse osmosis units with trained operators.

Chemical Processes (Chemical Reduction, Ozone-Peroxide)

Perchlorate is a highly oxidized compound (i.e., it has a strong affinity for electrons). One might therefore expect that perchlorate could be destroyed by adding a chemical reducing agent to convert its chlorine atoms to chloride, a harmless component of table salt. Unfortunately, the chemical reaction between perchlorate and commonly used reducing agents is too slow to be of practical use. Perchlorate may react with more exotic reducing agents, such as titanium, vanadium, molybdenum, or ruthenium, but these chemicals are likely to be too unstable or toxic to be practical for water treatment. Catalysts that could selectively speed the destruction of perchlorate have not been identified.

Ozone-peroxide treatment appears to have minimal effect on perchlorate in water, but ozone-peroxide followed by liquid phase carbon treatment has been shown to remove perchlorate from groundwater at a water supply well in the San Gabriel Valley. EPA is planning additional tests to evaluate the long-term effectiveness, reliability, and cost of the process. AWWARF may also fund additional evaluations of this process as part of its \$2 million federally funded perchlorate treatment research program.

Biochemical Processes (Anaerobic Biochemical Reduction)

To date, more effort has been directed at developing an anaerobic biochemical reduction process than any other treatment option. In the biochemical reduction process, microbes are used to

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convert perchlorate to a less toxic or innocuous form. Microbes have been used for decades in the treatment of some drinking water supplies, as part of a process known as slow sand filtration.

The Air Force Research Laboratory, Materials and Manufacturing Directorate began development of biochemical reactor systems for the treatment of high level perchlorate-contaminated wastewater, i.e. 1000 to 10,000 parts per million (ppm), more than eight years ago. A production-scale, continuous-stirred-tank-reactor system began treating wastewater from rocket motor production operations in Utah in 1997. Applying the same concept, pilot-scale tests of an anaerobic fluidized bed bioreactor were completed at the Aerojet Superfund site near Sacramento, California in 1996. The tests demonstrated that a bioreactor could reduce perchlorate concentrations in groundwater from over 5000 ppb to the low hundreds of ppb. A 4000-gallon per minute (gpm) flow-through bioreactor is expected to be online by late 1998 to treat contaminated groundwater before recharge to the aquifer.

Additional pilot-scale tests were recently completed by the Baldwin Park Operable Unit Steering Committee at one of the San Gabriel Valley Superfund sites, where groundwater contaminated with approximately 150 ppb perchlorate must be treated. Results from the San Gabriel Valley tests are encouraging; perchlorate has been reduced to nondetectable levels. The bioreactor also removed nitrate, which is present in the aquifer at 20 to 30 ppm (as NO₃). Larger-scale testing at 500 to 1000 gpm will continue later in 1998 at a perchlorate-contaminated drinking water supply well in the San Gabriel Valley. Ultimately, a perchlorate treatment facility with the capacity to treat 20,000 gpm is expected to be built with some or all of the treated water supplied to local drinking water utilities. Although bioreactors appear capable of removing low level perchlorate contamination from drinking water supplies, the cost, reliability, and public acceptance of this technology are not well established.

The Air Force Research Laboratory has also initiated an effort to isolate enzymes from the microorganism responsible for perchlorate reduction. If this effort is successful, enzymes might be used in a fixed-bed reactor system to selectively remove perchlorate over a range of concentrations.

Summary

Only in the last year has a substantial effort been directed at the development of perchlorate-removal technologies that could potentially be used to treat perchlorate-contaminated drinking water supplies. By late 1998 or early 1999, pilot-scale studies of two or three promising technologies will have been completed, and performance data from a full-scale anaerobic biochemical treatment system should be available. In 2001, results from the \$2 million AWWARF research effort will also become available.

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Perchlorate:

The Las Vegas Valley Experience

Kay Brothers

Kim Zikmund

Southern Nevada Water Authority



Southern Nevada Water Authority

- 💧 City of Las Vegas
- 💧 City of Henderson
- 💧 Clark County Sanitation District
- 💧 City of North Las Vegas
- 💧 Boulder City
- 💧 Las Vegas Valley Water District
- 💧 Big Bend Water District



Perchlorate: The Las Vegas Valley Experience

- I. Background of Perchlorate Manufacture & Use
- II. Identification of Perchlorate in Water
- III. Public Notification
- IV. Taking Action



Ammonium Perchlorate Production

- ◆ Kerr McGee

- ◆ Began 1953

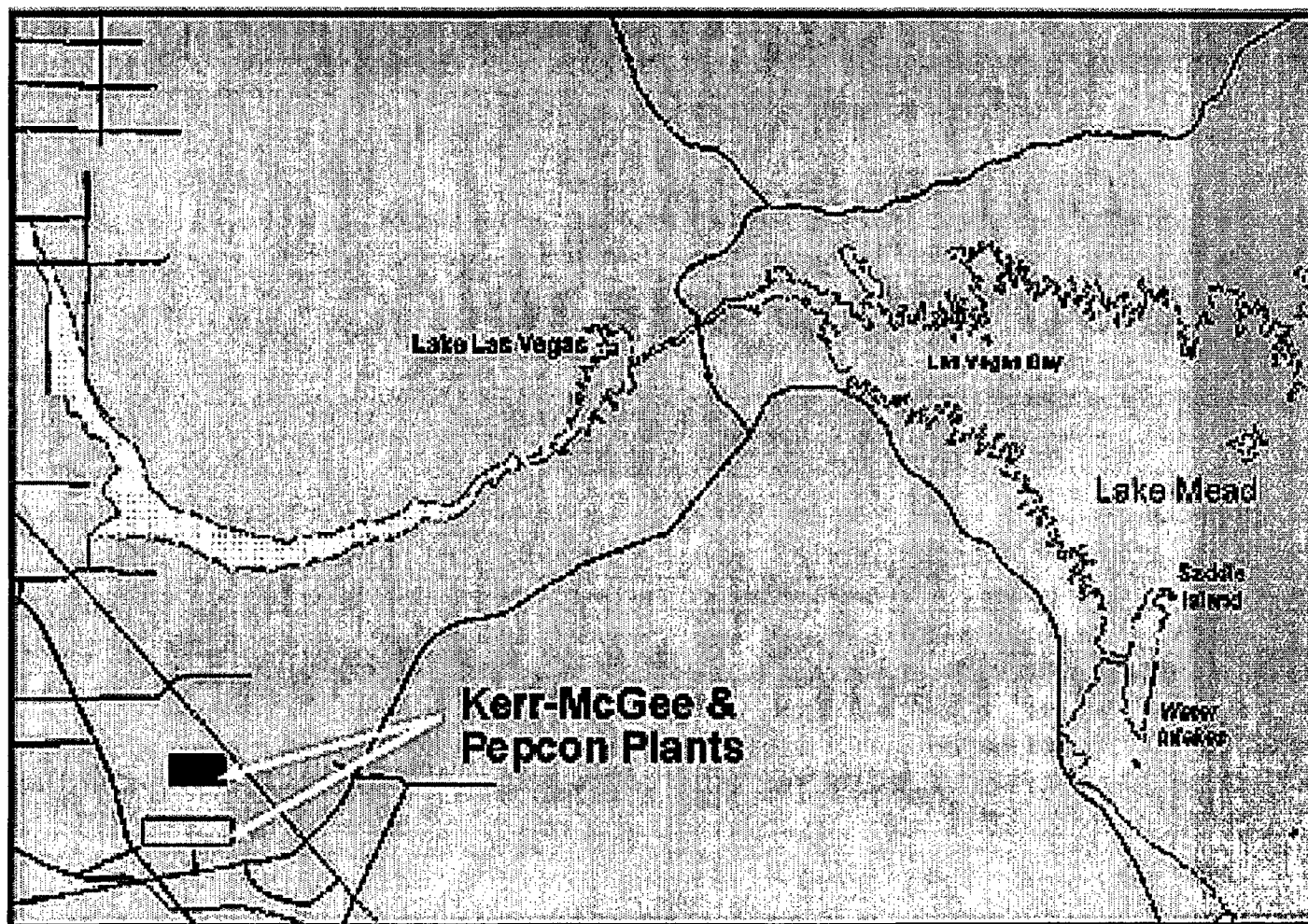
- ◆ Ending Summer 1998

- ◆ American Pacific (formerly PEPCON)

- ◆ Began 1958

- ◆ Ended May 1988

Perchlorate Sources





Ammonium Perchlorate Use

- 💧 Oxidizer component in solid propellant for rockets and missiles (90%)
- 💧 Production of fireworks, matches, pyrotechnics and analytical chemistry (10%)
- 💧 Previously used in fertilizers
- 💧 35+ states have facilities (150) that use perchlorate



Identification of Perchlorate in Water

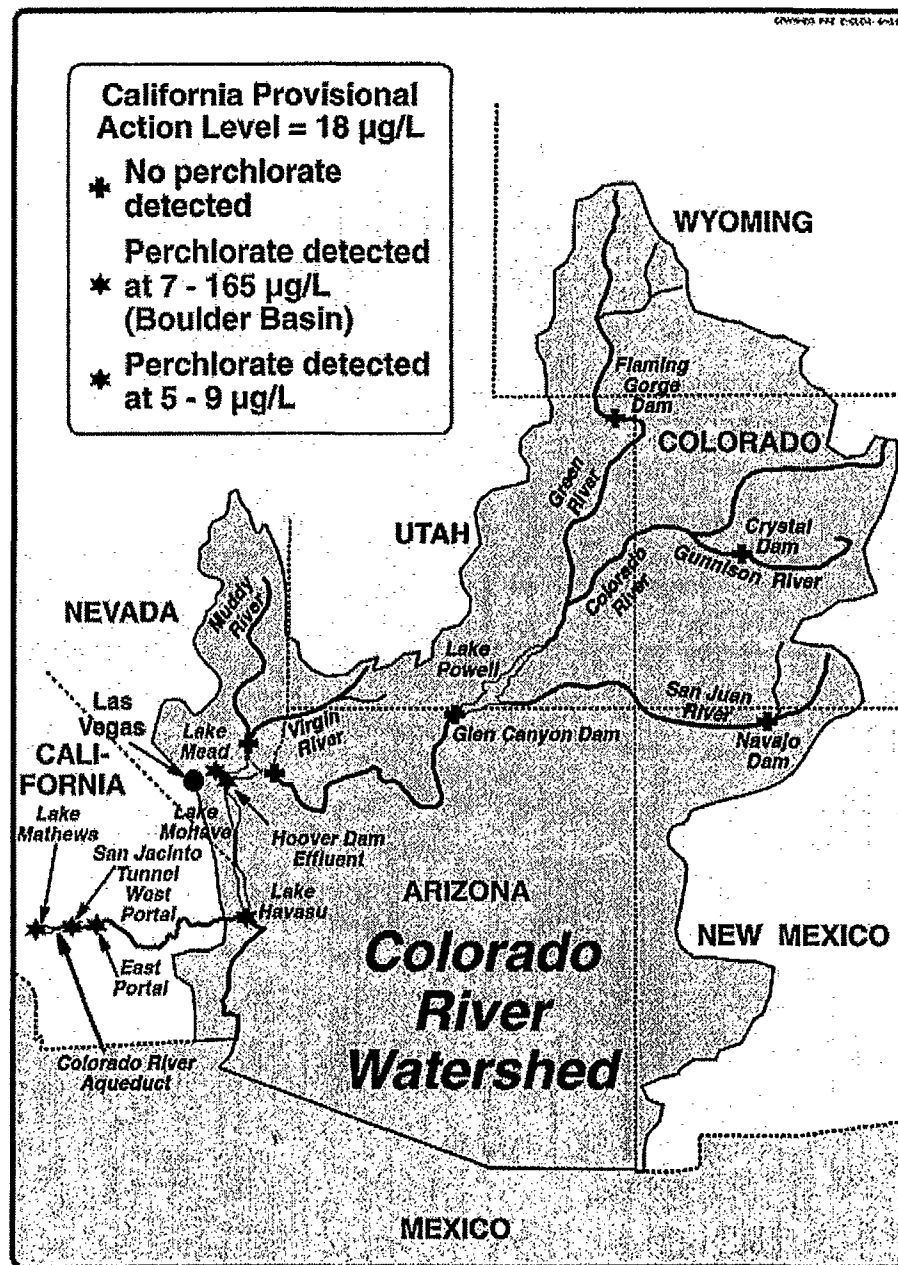
- Not required as standard sampling parameter (not on any CERCLA, RCRA, etc. list)
- April 1997 - 4 ppb detection limit (previously 400 ppb)



A Courtesy Call

- ◆ June '97 Metropolitan Water District calls SNWA
- ◆ Raw system water sample tested for perchlorate
- ◆ Notified SNWA of plans to determine source of perchlorate by sampling throughout Colorado River System

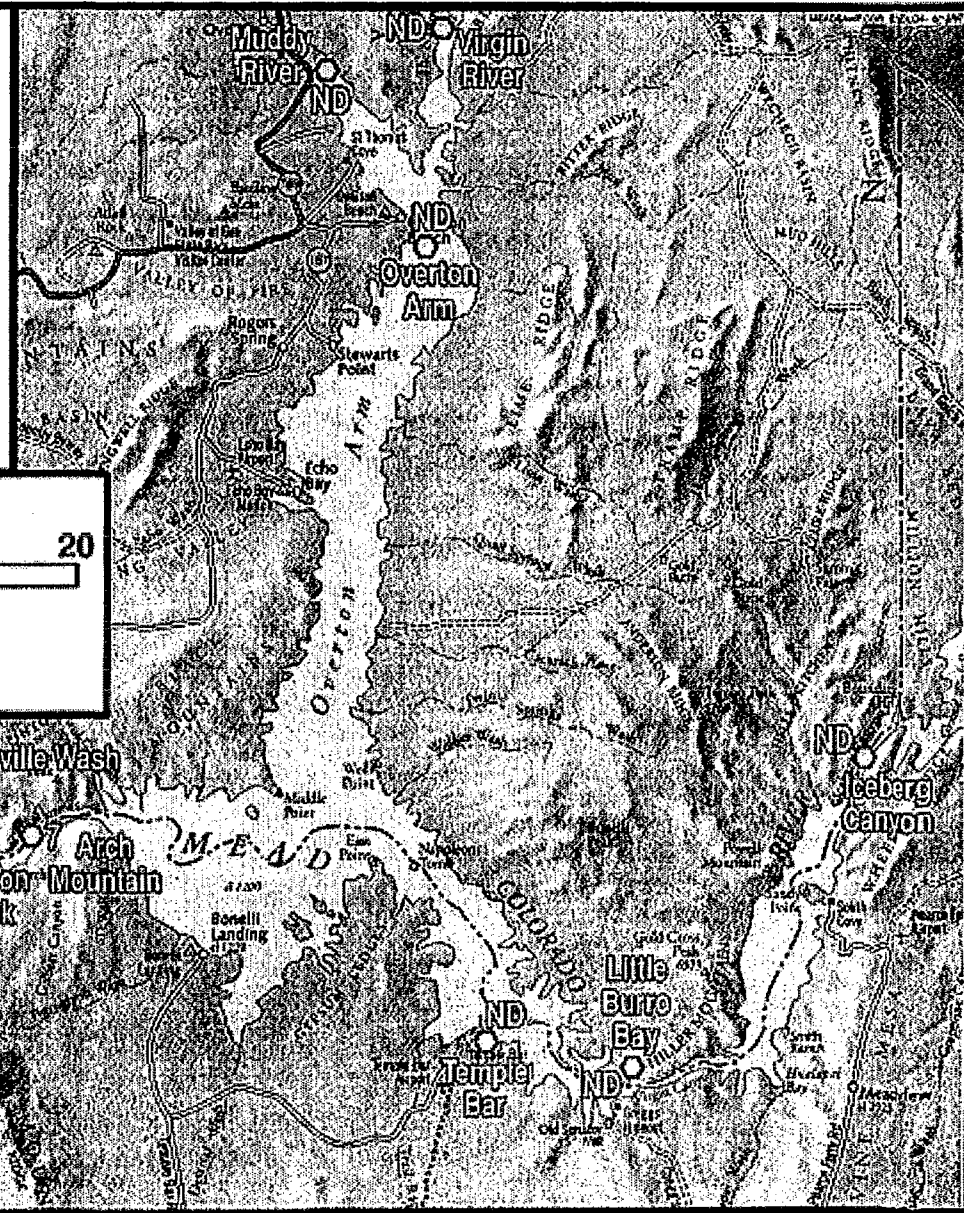
*Map courtesy of
MWD*



**Perchlorate Detection in the
Colorado River Watershed**

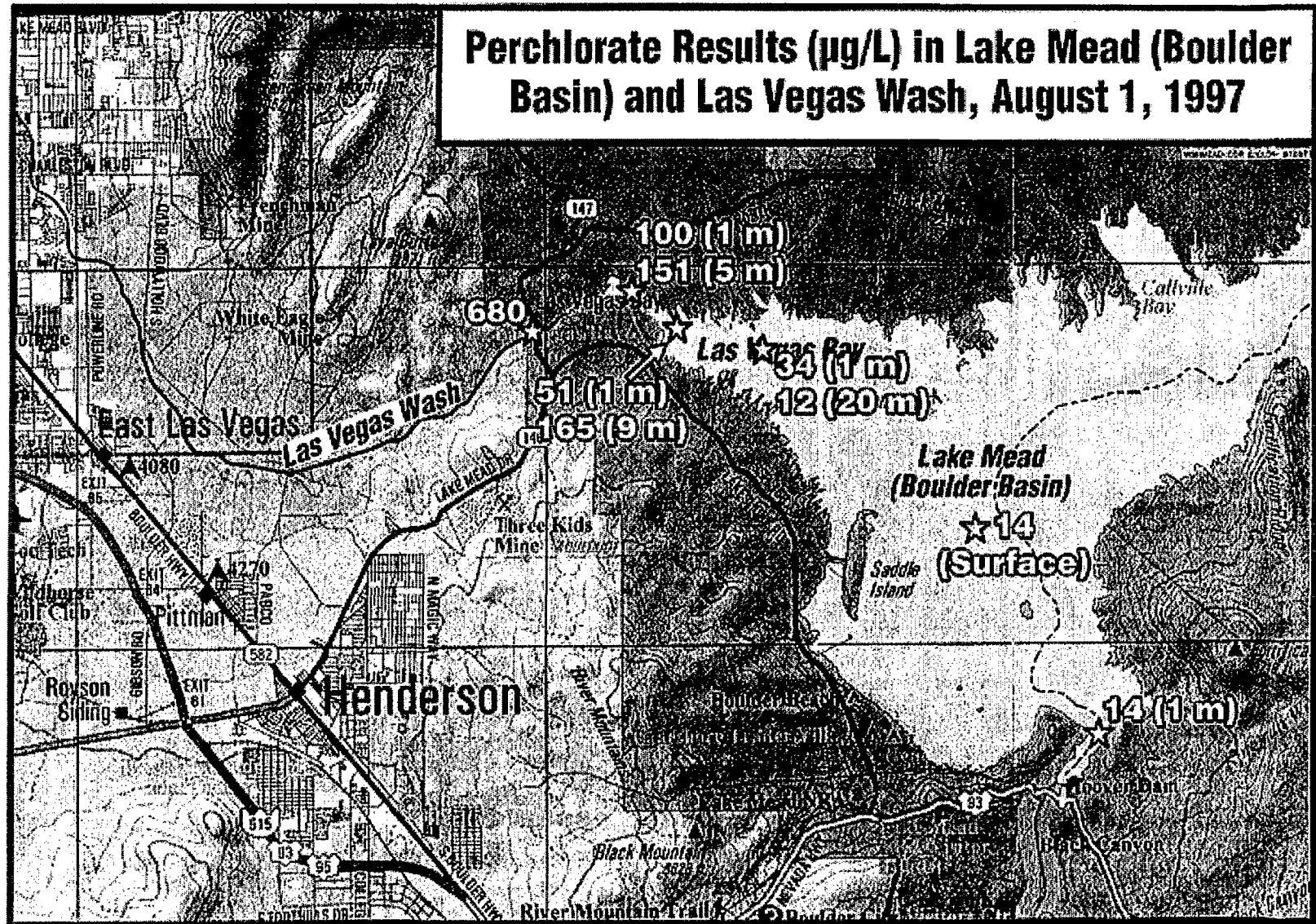
Sampled July 23 & 24, 1997

Las Vegas Wash--86	Arch Mountain--7
Las Vegas Bay--42	Overton Arm--ND
Black Island--19	Muddy River--ND
Hoover Dam--15	Virgin River--ND
Beacon Rock--12	Temple Bar--ND
Callville Bay--12	Little Burro Bay--ND
Callville Wash--11	Iceberg Canyon--ND
West End Wash--11	(ND = Not detected)



Map courtesy of MWD

Perchlorate Results ($\mu\text{g/L}$) in Lake Mead (Boulder Basin) and Las Vegas Wash, August 1, 1997



Map courtesy of MWD



Public Notification: Announce the Findings



Methods of Notification

- ◆ Press conferences
- ◆ Fact sheets/newsletter
- ◆ Coordinated media coverage
- ◆ Lake Mead Water Quality Forum updates
- ◆ Water Quality Citizens Advisory Committee

Press Conferences



August 18



October 10

Fact Sheets/Newsletters

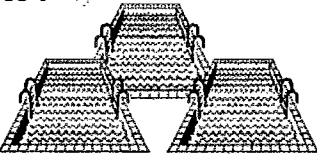
HOT
Water Issues

*Southern Nevada
Water Authority
Sept. 97*

Yes, our water is safe to drink!

The following questions...

What is perchlorate?



Is it a threat to my health?

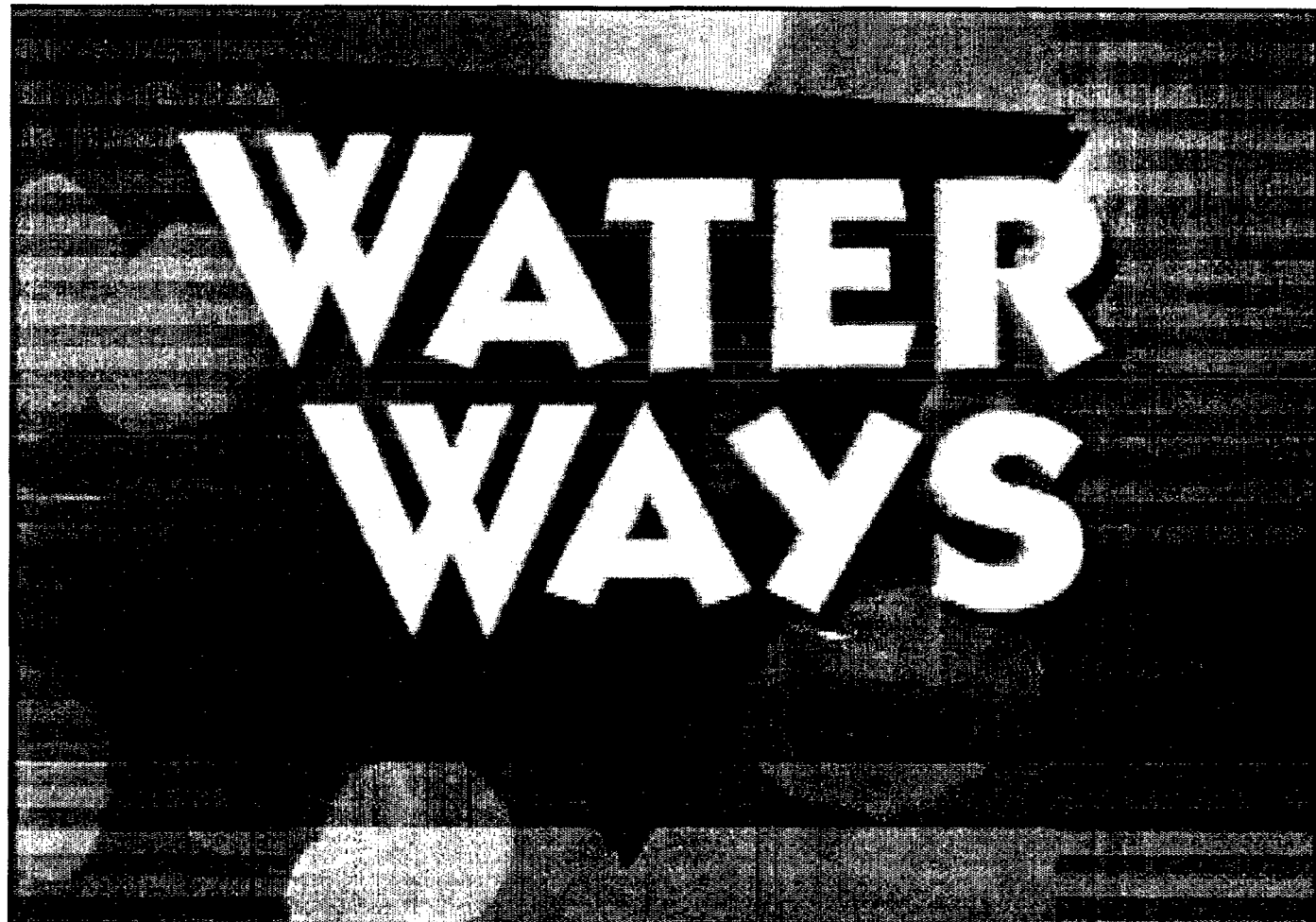
Where does my water come from?

Is it safe for swimming, etc?

Should I boil my water?

Does reverse osmosis get rid of it?

Coordinated Media Coverage



Updates to LMWQF

Perchlorate Values in SNWS Supply

July	11	11
September	7	4
October	< 4	5
November	< 4	5
December	16	14
January	14	11
February	11	11
March	8	8
April	11	10

*Detection Limit 4 ppb

Water Quality Citizen's Advisory Committee



- ◆ Established 8/20/97
- ◆ Bring in experts for committee meeting
- ◆ Additional positive and coordinated media coverage
- ◆ Group kept informed on all current developments



Taking Action

Local

Regional

National



Taking Action: Local

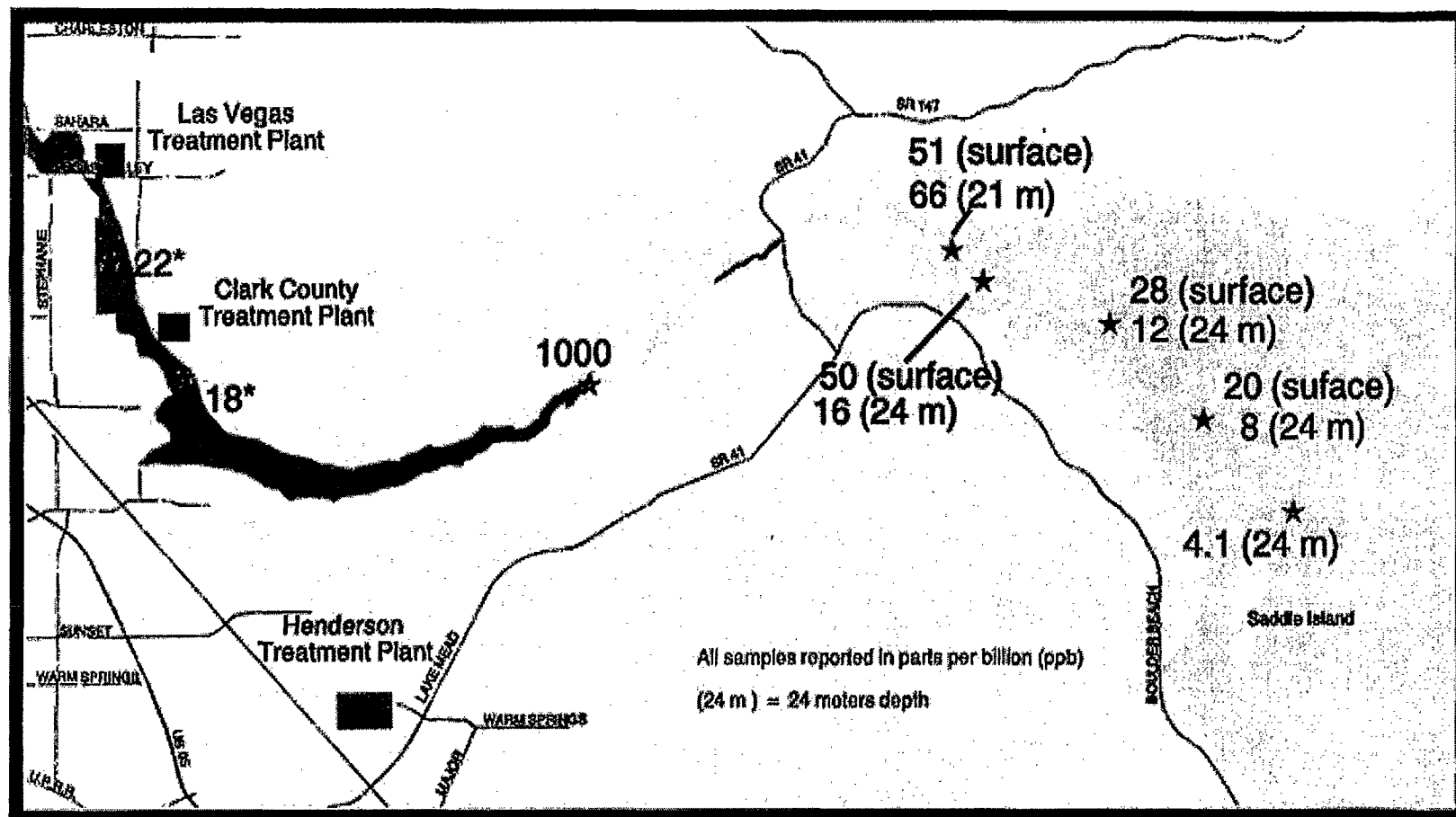
- ◆ Water quality sampling continues
- ◆ October 1997 - NDEP announces 3-phase remediation approach
 - ◆ Identify contamination sources (completed)
 - ◆ Site characterization & flow path identification (completed by summer of 1998)
 - ◆ Design/implement remediation plan (target: Dec. 1998)



Taking Action: Regional

Perchlorate Issues Group

- ◆ Metropolitan Water District of So. Calif.
- ◆ East Valley Water District (CA)
- ◆ Main San Gabriel Basin Watermaster (CA)
- ◆ San Bernardino Valley Municipal Water District (CA)
- ◆ Southern Nevada Water Authority



Results of Perchlorate Samples by SNWA 14 August 1997



Taking Action: National

- ◆ AWWA Research Foundation
- ◆ Perchlorate Study Group
- ◆ Interagency Perchlorate Steering Committee
- ◆ Ongoing health-effect research
 - ◆ 8 studies underway
 - ◆ Results reviewed 9/98 by IPSC & EPA
 - ◆ Results available for external review 10/98



Dealing with Perchlorate Contamination in the San Gabriel Valley

Carol Williams
Main San Gabriel Basin
Watermaster

Main San Gabriel Basin

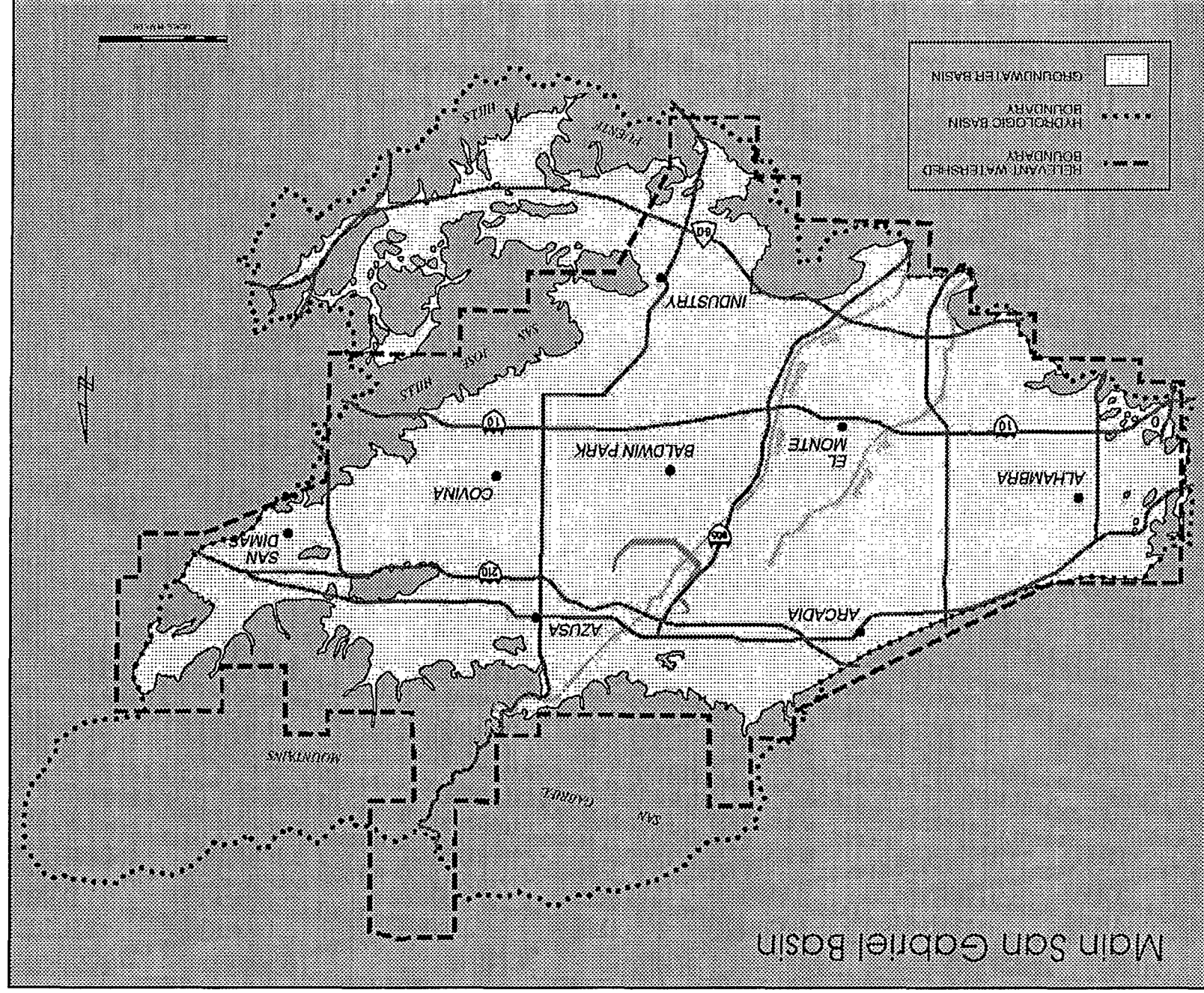
- Adjudicated groundwater basin
 - ◆ Watermaster is court-appointed basin manager
 - ◆ 60 active pumpers (municipal & industrial)
- Located in eastern Los Angeles County
 - ◆ overlies San Gabriel Valley
 - ◆ surface area of 167 square miles
- Primary source of drinking water for 1.5 million people

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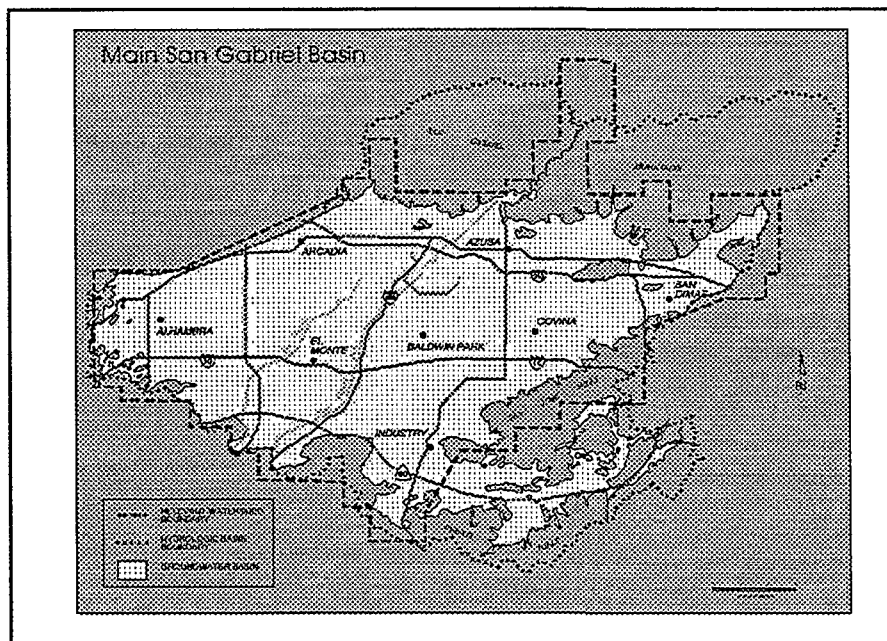
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Basin Characteristics & Operations

- Contains about 8 million acre-feet of water
- Operating range of 400,000 - 500,000 AF
- Annual production: \pm 270,000 AF
- Average annual recharge:
 - ◆ 100,000 - 150,000 AF “local” water
 - ◆ 25,000 - 40,000 AF imported water



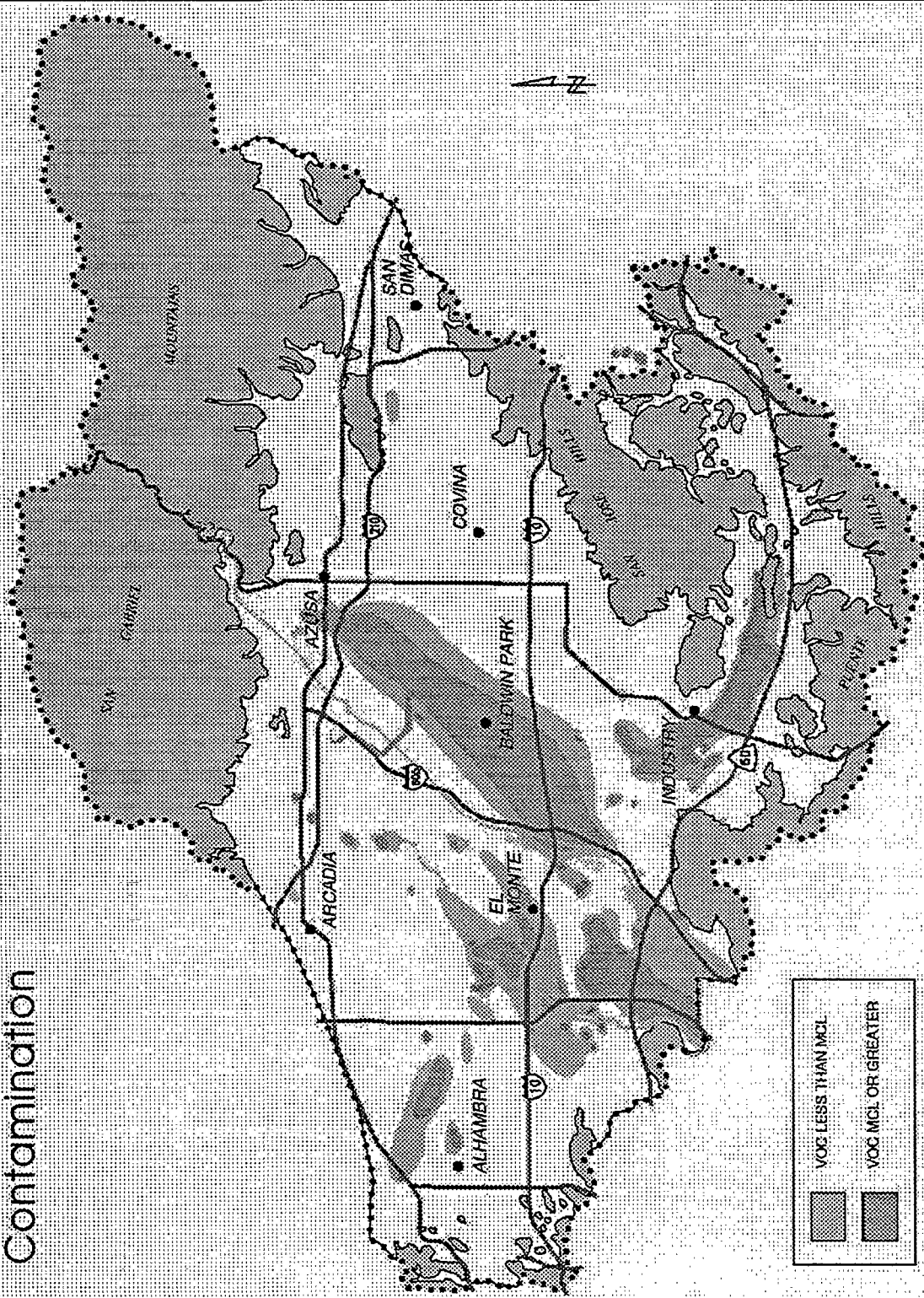
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Basin Water Quality Issues

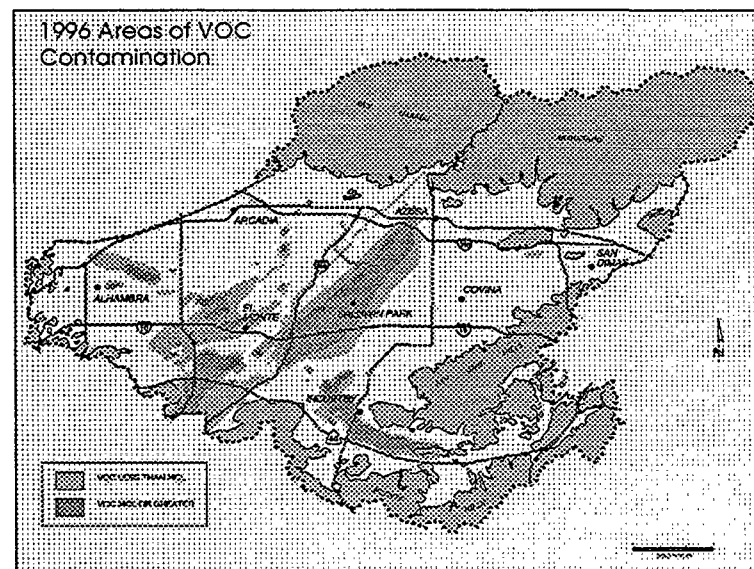
- Volatile Organic Compounds
 - ◆ EPA Superfund site
- Nitrates
 - ◆ eastern portion of Basin
 - ◆ from past agricultural practices

1996 Areas of VOC Contamination

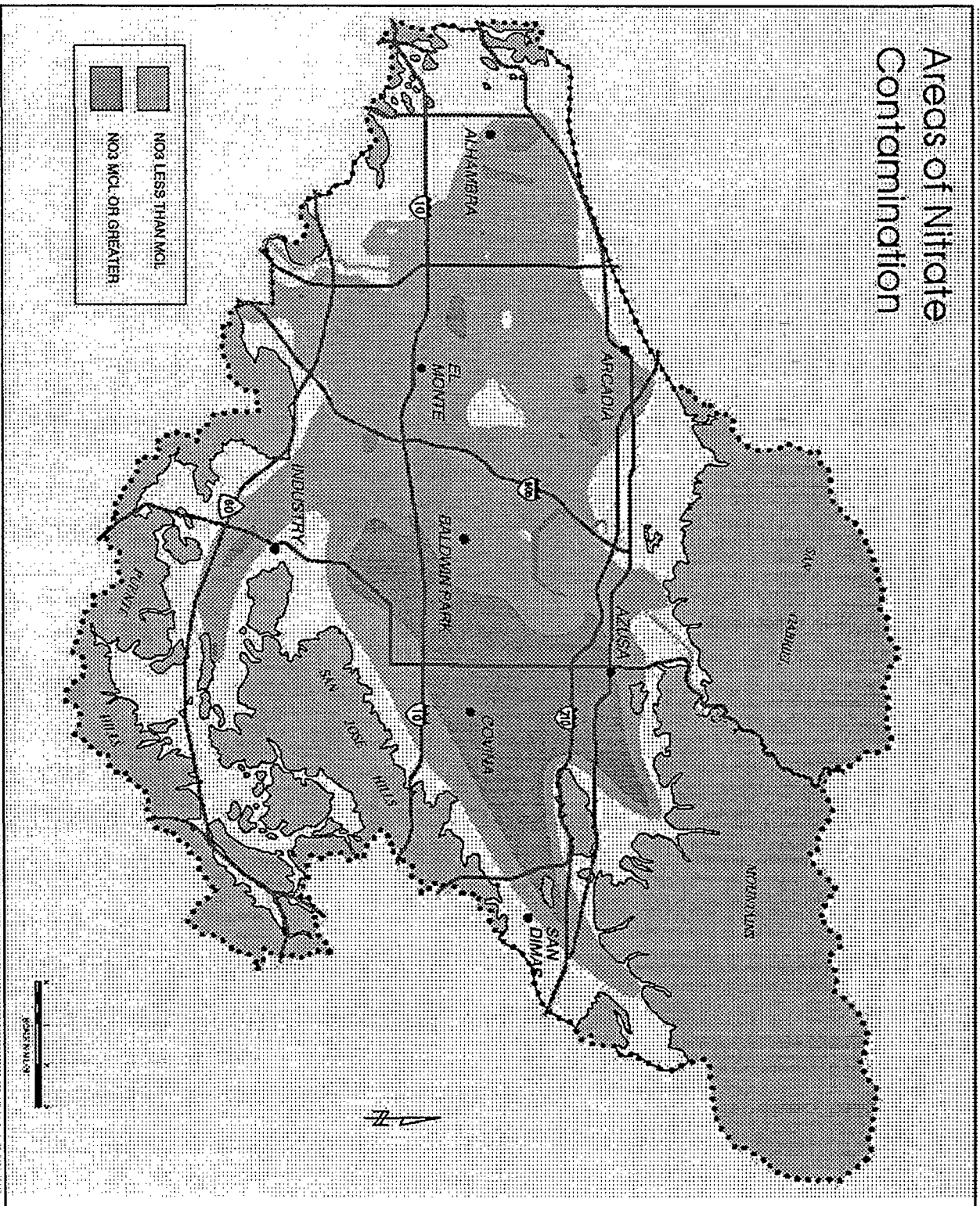


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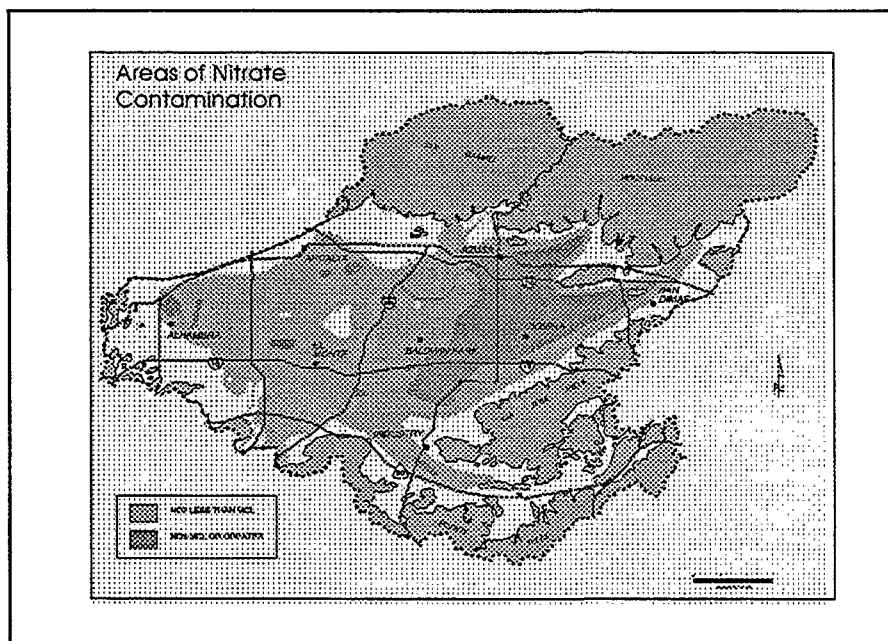


Areas of Nitrate Contamination



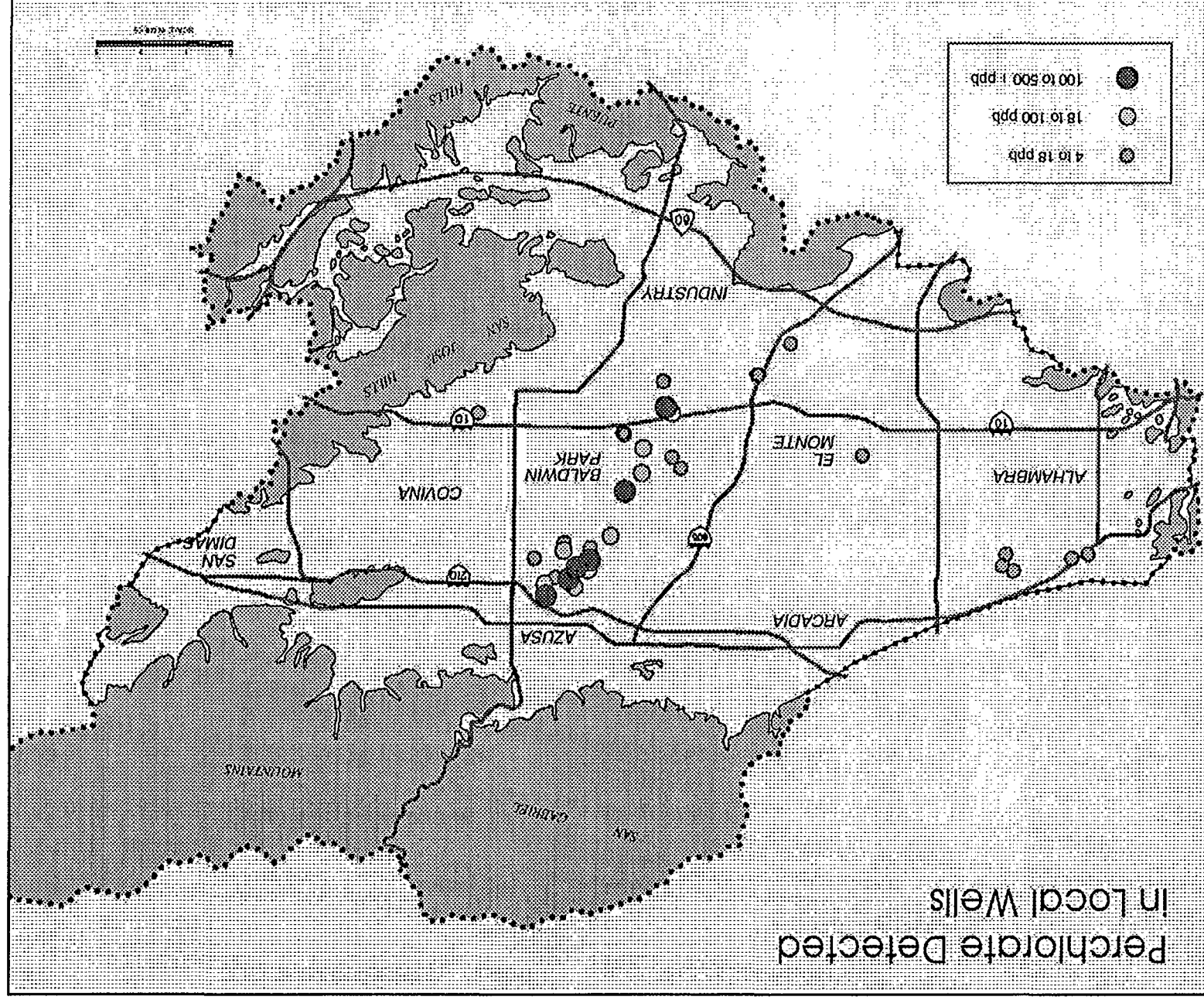
Perchlorate Contamination

- DHS first discovered in Basin in May 1997
- DHS & Watermaster coordinated initial sampling program to determine extent of contamination
- “Footprint” of perchlorate contamination matched largest Superfund sub-area
 - ◆ highest concentrations in production wells at leading edge of VOC plume
- Watermaster’s subsequent basin-wide testing found no other significant areas of contamination



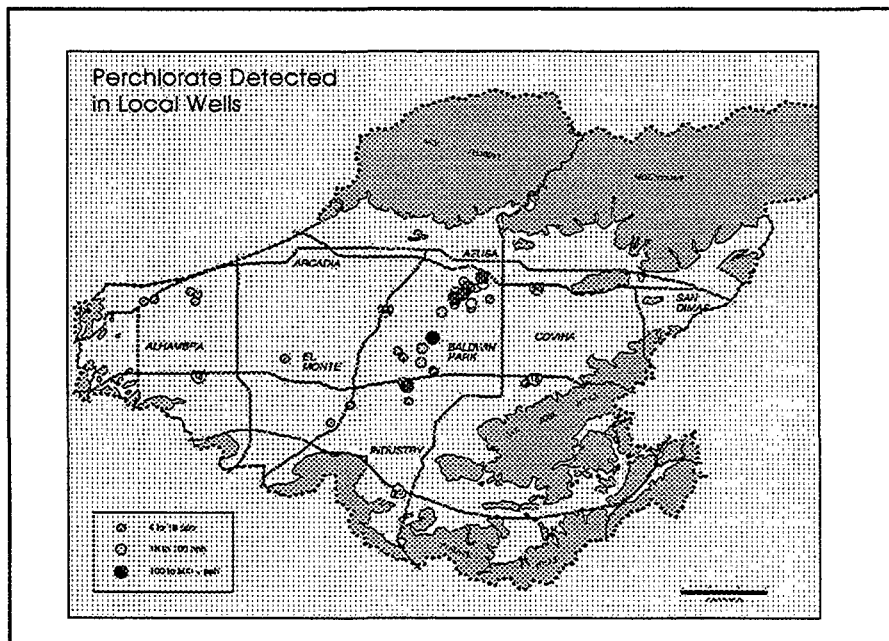
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Water Purveyor Impact

- One water district lost all of its three wells
- An investor-owned utility lost one well
- Both purveyors had constructed air strippers to remove VOCs from water at those sites
- Basin-wide, 8 wells exceeded provisional action level of 18 ppb
 - ◆ 4 (above) were immediately shut down
 - ◆ 2 are being treated/blended
 - ◆ 2 inactive due to other contamination



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Superfund Cleanup Impact

- VOC treatment project plans halted due to perchlorate
- Perchlorate treatment must be incorporated into project
- Project costs may increase significantly

Seeking Solutions

- Cost-effective treatment solution needed
- Watermaster formed Perchlorate Coordinating Team to share information, pool research resources
 - ◆ local, regional affected water agencies
 - ◆ regional, state & federal regulatory agencies
 - ◆ potentially responsible parties

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Current Activities

- Watermaster is funding two studies:
 - ◆ ion-exchange evaluation through Montgomery Watson (lab and pilot scale)
 - ◆ demonstration of Calgon/AST ion-exchange facility
- Aerojet/PRPs are evaluating biological removal process
 - ◆ pilot project planned for water district well

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Bioreduction of Perchlorate in Groundwater

129

Michael Girard
Aerojet Environmental Operations

History

- ◆ Aerojet has been manufacturing rockets and explosives since the mid 1940's at sites in Northern and Southern California
- ◆ The use of ammonium perchlorate in solid rocket fuels contributed to current situation
- ◆ Both sites are designated CERCLA Superfund Sites

Northern California Site

- ◆ Located in Sacramento
- ◆ Soil & Groundwater contamination primarily VOC's, Perchlorate and NDMA
- ◆ Started treating groundwater for VOC's in 1981
- ◆ Perchlorate discovered in off-site drinking water supply wells in January 1997

Northern California Site

- ◆ Currently operating 5 Groundwater Extraction and Treatment (GET) Facilities
- ◆ Air strippers and UV oxidation combinations
- ◆ Treating ~ 8 million gallons per day
- ◆ 38 billion gallons treated to date

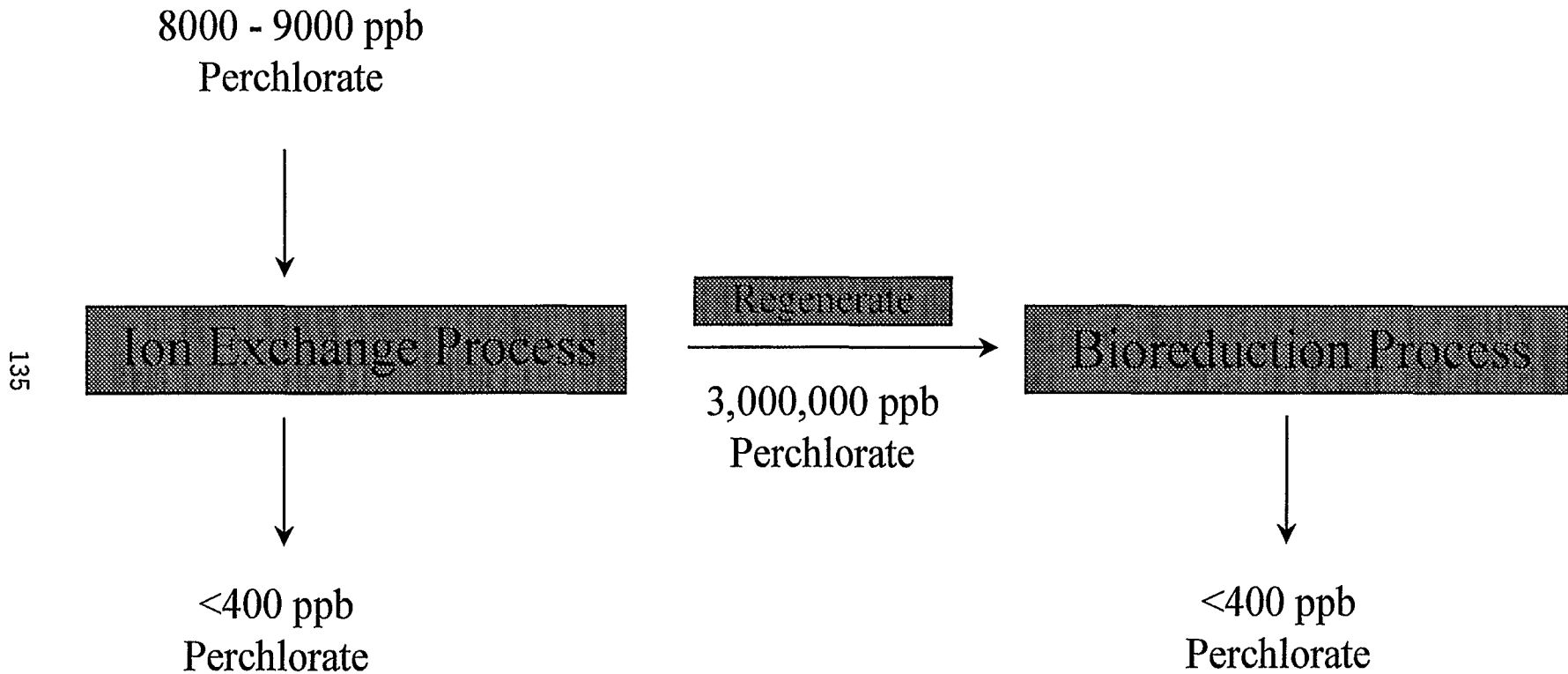
Northern California Site

- ◆ Began perchlorate treatment investigation 1993
- ◆ Literature search
- ◆ Feasibility studies on available technologies
- ◆ Ion exchange coupled with bioreduction of regenerate waste selected for laboratory and pilot testing

Ion Exchange / Bioreduction

- ◆ Treat effluent from GET F (air stripper)
- ◆ Ion Ex. influent 8000-9000 ppb perchlorate
- ◆ Pilot scale demonstration in 1994
- ◆ Analytical detection limits of <400 ppb
- ◆ Achieved >400 ppb effluent

Ion Exchange / Bioreduction



Ion Exchange / Bioreduction

♦ Limitations

- Ion Exchange generates contaminated waste stream
- Two systems required (Ion Ex / Biological)
- Cost
- Resin dynamics (CLO₄ Bleed / Resin Attrition)
- Handling concentrated perchlorate

Direct Bioreduction Process

- ◆ Eliminate ion exchange concentration step
- ◆ Treatment goal of <400 ppb
- ◆ Continuous flow fluidized carbon bed bio-reactor
- ◆ Recycle capabilities
- ◆ Automated feed systems with remote operation (unmanned)

Bioreduction Pilot Plant (1996)

- ◆ Influent 8000-9000 ppb perchlorate
- ◆ Sized for 30 gpm flow rate
- ◆ Residence time of ~12 min
- ◆ Demonstrated effluent <100 ppb perchlorate
(analytical method detection limit at the time)
- ◆ No addition of chemical contaminants into
the effluent other than chloride

Second Bioreduction Pilot Plant

- ◆ Aerojet Facility in Azusa, CA (San Gabriel Basin)
- ◆ Address Southern California situation
- ◆ Influent 50-100 ppb perchlorate
- ◆ Nitrate levels of 4-6 ppm
- ◆ Analytical detection capabilities now 4 ppb

Second Bioreduction Pilot Plant

- ◆ Located at the Aerojet Sacramento Facility
- ◆ Same configuration as first pilot system
- ◆ Tested various operating parameters and system enhancements
- ◆ Demonstrated systems capability to treat perchlorate to <4 ppb and nitrate to <100 ppb

Full Scale Treatment System

- ◆ Currently under construction in Sacramento
- ◆ Start-up in Sept 1998
- ◆ 4000 gpm as-built with 8000 gpm expansion capacity
- ◆ Treatment goal of <4 ppb
- ◆ Regulatory approval for re-injection into groundwater

Conclusion

- ◆ Bioreduction process proven successful at treating groundwater to <4 ppb
- ◆ No contaminated waste stream
- ◆ No added chemical contaminants to effluent
- ◆ Effluent treatment for microorganisms has decades of history

Contact

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Sacramento, CA 95813-6000

916.355.2945

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The Biochemical Reduction of Perchlorate at Low Concentrations in Water - Technology Application for Groundwater in San Gabriel Basin, California

John G. Catts, Ph.D., Harding Lawson Associates

Abstract

A biological treatment technology, previously tested at a pilot scale for reduction of perchlorate in water from concentrations of 10,000 ug/L to less than the historical 400 ug/L laboratory reporting limit has been tested for application at lower concentrations. This technology, a fixed film bioreactor using granular activated carbon operated as a fluidized bed, has proven successful in reducing perchlorate concentrations in groundwater from approximately 40 ug/L to a level less than the 4 ug/L analytical reporting limit. This pilot-scale test was also performed in the presence of 50 mg/L nitrate which was reduced to concentrations less than the 0.1 mg/L analytical reporting limit. The operating parameters which best represent destructive efficiency of perchlorate and nitrate were dissolved oxygen and oxidation reduction potential. Effluent from the bioreactor followed by filtration and disinfection (conventional treatment applied to surface water) should meet criteria for potable use. A Phase 2 Treatability Study, scheduled for 1998, will address several key issues related to the potable use of treated water including the characteristics of the source of microorganisms (inoculum), the acceptability of all additives for use in a drinking water supply, the effectiveness of filtration and disinfection, and disinfection by-products.

Introduction

In June 1997 the Baldwin Park Operable Unit (BPOU) Steering Committee in conjunction with Three Valleys Municipal Water District (TVMWD), the Metropolitan Water District of Southern California (MWDSC), and the U.S. Environmental Protection Agency (EPA), had completed conceptual design of a groundwater extraction and water supply project, and had begun the process of interviewing and selecting a contractor to design, build, and operate the project. The project, as conceived, was to extract approximately 20,000 gpm of groundwater from 5 locations to both remove chlorinated volatile organic compounds (VOCs) and control VOC plume migration. In addition to controlling VOC plume migration the project was also conceived to add a valuable conjunctive use component to local water supply operations. The treated water was to be delivered into the MWDSC Middle Feeder for public consumption. Seasonally available replacement water was to be purchased and recharged. This conjunctive use was to provide TVMWD and MWDSC with additional drought protection. All extracted water was to be piped to a central treatment plant where air stripping with vapor phase granular activated carbon was to be used to remove VOCs. At issue in June 1997 was the anticipated 20 to 25 mg/L of nitrate (as nitrate) that would be contained in the treated water. Although this concentration was well below the maximum contaminant level (MCL), it was significantly higher than concentrations of nitrate in water currently served by MWDSC.

In June 1997 concentrations of perchlorate ion, above the State of California Department of Health Services (DHS) provisional action level of 18 µg/L, were found in BPOU groundwater. Based on data from both monitoring and production wells the concentration of perchlorate in water produced by the BPOU extraction system will be between 50 and 100 ug/L. Before the project can move forward, the potential impact that perchlorate has on the conceptual project design must be evaluated. The presence of low concentrations of perchlorate in BPOU groundwater is particularly troublesome as there is no treatment technology that has been demonstrated to be effective in reducing concentrations of perchlorate to the provisional action level.

Fortunately, Aerojet-General Corporation (Aerojet) had, from 1994 to 1996, performed treatability studies to address concentrations of 8,000 to 10,000 µg/L in groundwater at their Sacramento facility. The goal of these studies was to produce effluent containing less than 400 µg/L, the analytical reporting limit at the time, and to recharge this treated groundwater on site. The Aerojet technology is best described as a biochemical reduction process using a fixed film bioreactor. The fixed film is attached to granular activated carbon operated as a fluidized bed. To maintain microorganism activity nutrients (nitrogen and phosphorus) are added to the influent stream. In addition an organic substrate (ethanol) is added. The Aerojet treatability study successfully produced effluent with perchlorate concentrations less than the 400 µg/L analytical reporting limit.

A comparison of available data on a range of candidate treatment technologies confirmed that this biochemical reduction technology was not only the technology which would probably be most readily proven for application with San Gabriel Basin groundwater but that this technology would likely be the most cost-effective. Therefore, the biochemical reduction technology developed by Aerojet was chosen for treatability study.

Project Goals

Before discussing the specific objectives of the subject treatability study it is necessary to review the water quality goals for the larger BPOU project. As the goal of this project is to produce water of potable quality all state and federal water quality criteria must be met. More specifically because this technology involves biological treatment using an innovative treatment technology that must be permitted by the California Department of Health Services (DHS) several specific objectives must be met. These include:

- The delivered water must be free of pathogens. Therefore, either the inoculum must lack pathogens, pathogens must be flushed from the bioreactor before effluent is diverted for potable use, or the water must be disinfected before delivery.
- Ethanol must be absent in effluent. Either the bioreactor must produce water with non-detectable ethanol or an additional treatment unit must remove residual ethanol.
- The bioreactor must not create unwanted by-products. This would include either by-products resulting from the presence of VOCs (e.g., vinyl chloride) in the groundwater or other dissolved organic compounds which might result from the disinfection process.
- Any additives that are needed for operation of the bioreactor must be certified for use in drinking water systems.
- To receive a permit for continuous operation bioreactor controls must assure destructive performance and demonstrate safety features to protect customers.

Scope of Treatability Study

There are several important differences between objectives of the previous treatability studies performed by Aerojet in Sacramento and the those of the BPOU project. First, the flow rate of the Sacramento treatability study was 0.1% of that needed in San Gabriel Basin. Second, the influent perchlorate concentration was over 100 times that expected in San Gabriel Basin. Third, the pilot system was not designed to achieve nor did it achieve effluent perchlorate concentrations less than the 18 µg/L provisional action level. Finally the previous testing was not designed to deliver potable water.

The purpose of this treatability study was to perform pilot-scale treatability testing of the biochemical reduction technology specifically for application in San Gabriel Basin. In the planning stage it was decided that pilot-scale testing would be performed in two phases. The first phase was designed to achieve the specific goals described below. In the second phase, scientific and engineering data needed to design and construct a full-scale treatment system are to be collected. There are several reasons that the treatability study is to be performed in two phases. Expertise and equipment were available at Aerojet's Sacramento site such that the previously used pilot-scale system could be quickly reassembled, use of this system which proved successful at higher influent concentrations would minimize treatability study variables, and initiation of a treatability study in San Gabriel Basin would necessitate negotiations and agreements with water purveyors which would likely delay the start of needed testing. Because the BPOU project is on hold until a treatment technology for perchlorate is proven timing is critical.

The primary goal of the Phase 1 Treatability Study was to determine if this technology would be effective for the low concentration to be encountered in San Gabriel Basin and deliver potable water. Specifically the objectives for the Phase 1 study were: 1) to treat water with a low influent concentration (30 to 100 µg/L) of perchlorate and produce an effluent with less than 18 µg/L perchlorate and, if possible, less than the 4 µg/L reporting limit; 2) remove nitrate concentrations representative of San Gabriel Basin groundwater; 3) use an alternative source of microorganisms; and 4) test treatment plant effluent for parameters used to test for potability of water.

To achieve these objectives a well which consistently produces water containing both perchlorate and nitrate at concentrations which are representative of those which will be encountered when the BPOU project comes on-line was selected.

The remainder of this paper provides a summary of the finding from the Phase 1 Treatability Study performed from November 1, 1997 through March 27, 1998 at Aerojet's Sacramento facility. A final Phase 1 Treatability Study Report will be available in June 1998. Planning has begun for a Phase 2 Treatability Study to be performed at a well site in the San Gabriel Basin.

Objective 1 - Destruction of Low Concentrations of Perchlorate

Concentrations of perchlorate from the well selected for pumping were approximately 40 µg/L. The Phase 1 bioreactor demonstrated that the system can consistently and reliably produce effluent containing concentrations of perchlorate less than the analytical reporting limit of 4 µg/L. Destructive performance of at least 90 percent was achieved. Bioreactor performance was strongly dependent upon the dissolved oxygen in the influent and the hydraulic retention time in the bioreactor. The profile of dissolved oxygen across the bioreactor and oxidation reduction potential of bioreactor influent and effluent have been chosen as the operating parameters which best predict bioreactor performance. Performance was strongly dependent on the ethanol concentration in the reactor influent. In addition it was determined that minimum concentrations of nutrients must be available to sustain microorganism populations.

Objective 2 - Destruction of Nitrate

Concentrations of nitrate in the source well ranged from 40 to 50 mg/L as nitrate. The study demonstrated that bioreactor effluent did not contain detectable concentrations of nitrate (reporting limit of 0.45 mg/L as nitrate). A 99 percent nitrate destruction efficiency was achieved. It was noted that maximum nitrate destruction was consistently achieved before complete destruction of perchlorate was achieved.

Objective 3 - Alternative Source of Microorganisms

Prior treatability testing used an inoculum of wastewater treatment plant sludge. To minimize the potential for introduction of pathogens into the bioreactor, a source of microorganisms from the food processing industry was selected. This waste from the processing of baby food proved to contain the necessary microorganisms. A characterization of this source of microorganisms will be performed as part of the Phase 2 Treatability Study.

Objective 4 - Potable Water Quality

Effluent from the bioreactor was tested several times for the full range parameters required by DHS for drinking water supplies. Results show that with filtration and disinfection the water should meet potable water quality criteria, however such testing was not performed and therefore this conclusion was not confirmed. Addition of these unit processes are planned for the Phase 2 Treatability Study and the full BPOU project. The specific technologies for accomplishing filtration and disinfection during the Phase 2 treatability study have not yet been selected.

Optimization of Operating Parameters

An unstated goal of the Phase 1 Treatability Study, assuming the above goals were achieved, was to generate the data necessary to design a Phase 2 Treatability Study, which would be performed in the San Gabriel Basin. These design data include influent concentrations of required additives (phosphorus, nitrogen, and ethanol), reactor flow rate and hydraulic retention time, and identification of monitoring parameters and tolerances that would ensure proper bioreactor performance.

In the course of establishing a stable system operation and processing performance data, it was learned that the profile of dissolved oxygen across the reactor and the oxidation reduction potential within the reactor were the two monitoring parameters which best predict bioreactor performance. Dissolved oxygen must be depleted early enough in the reactor flow path to a level of 0.1 to 0.2 mg/L to allow sufficient hydraulic retention time under these anoxic conditions to cause complete destruction of perchlorate and nitrate.

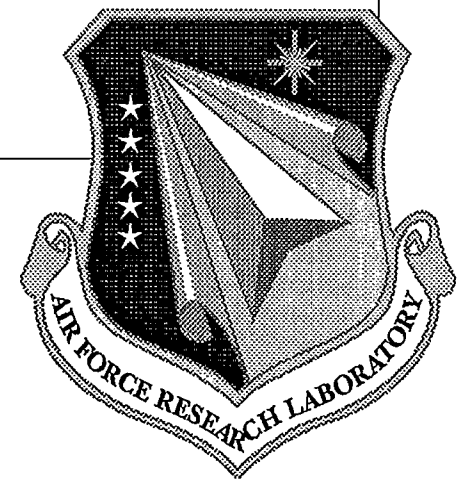
With respect to concentrations of nutrients, a minimum threshold level is necessary. Once that level is exceeded, excess nutrient is discharged in treatment plant effluent. Regarding influent concentrations of ethanol, a relatively narrow operating range is required (75 -100 mg/L). Above this working range, concentrations in excess of the 5 mg/L analytical reporting limit were present in the effluent. If concentrations of ethanol exceeded 200 mg/L clumping of the granular activated carbon occurred and bed fluidization degraded resulting loss of destructive performance for nitrate and perchlorate. At ethanol concentrations of 50 mg/L or less, destructive performance also degraded

Summary

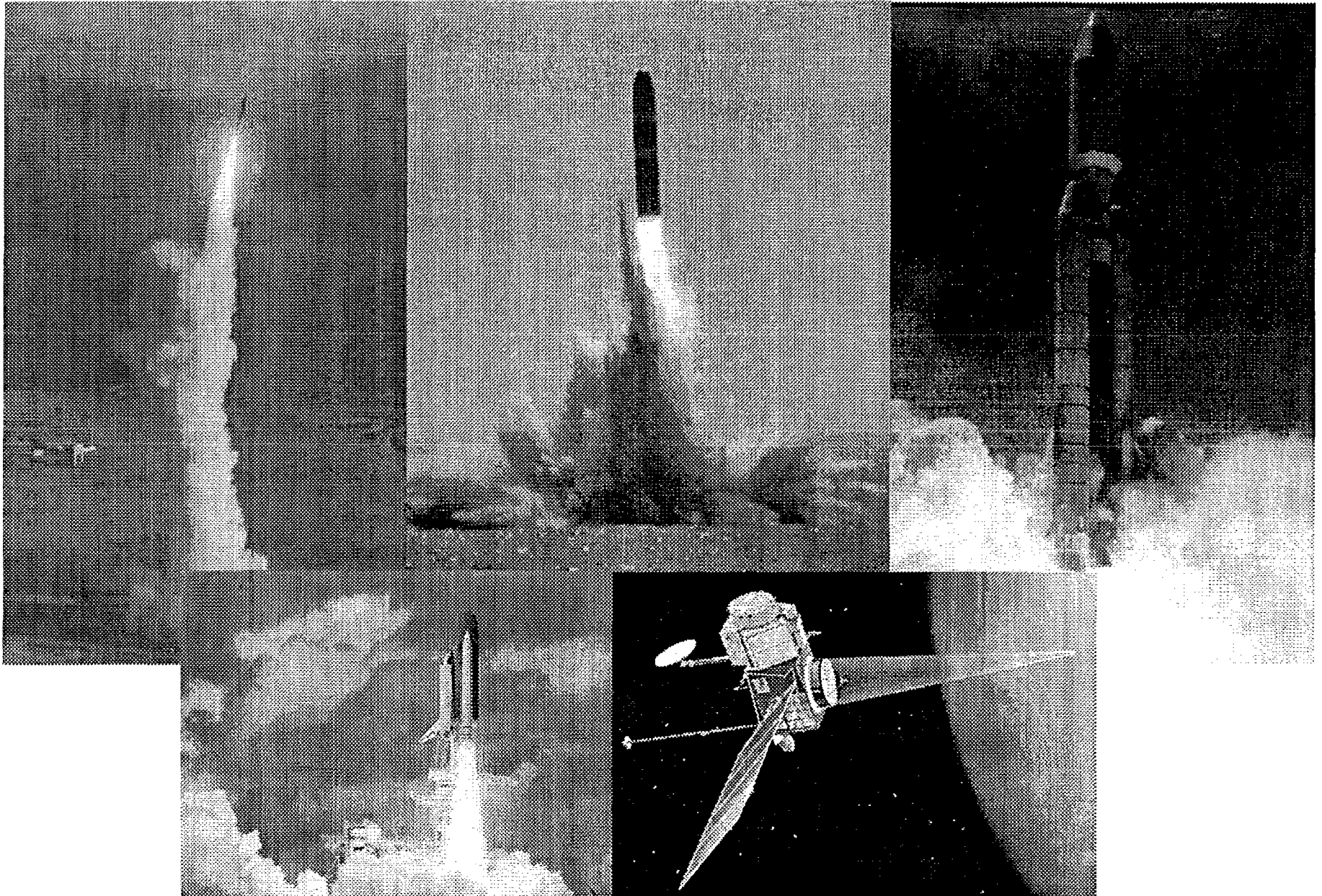
A biological treatment technology which causes biochemical reduction of perchlorate and nitrate was tested for application in San Gabriel Basin, California. This technology is a fixed film bioreactor using granular activated carbon operated as a fluidized bed. The Phase 1 Treatability Study produced effluent that was less than the 4 ug/L and 0.1 mg/L analytical reporting limits for perchlorate and nitrate respectively. A Phase 2 Treatability Study is planned for San Gabriel Basin in 1998 to collect additional data to support potable use of the effluent and to collect design data necessary to implement the previously conceived groundwater extraction, treatment, and water supply project.

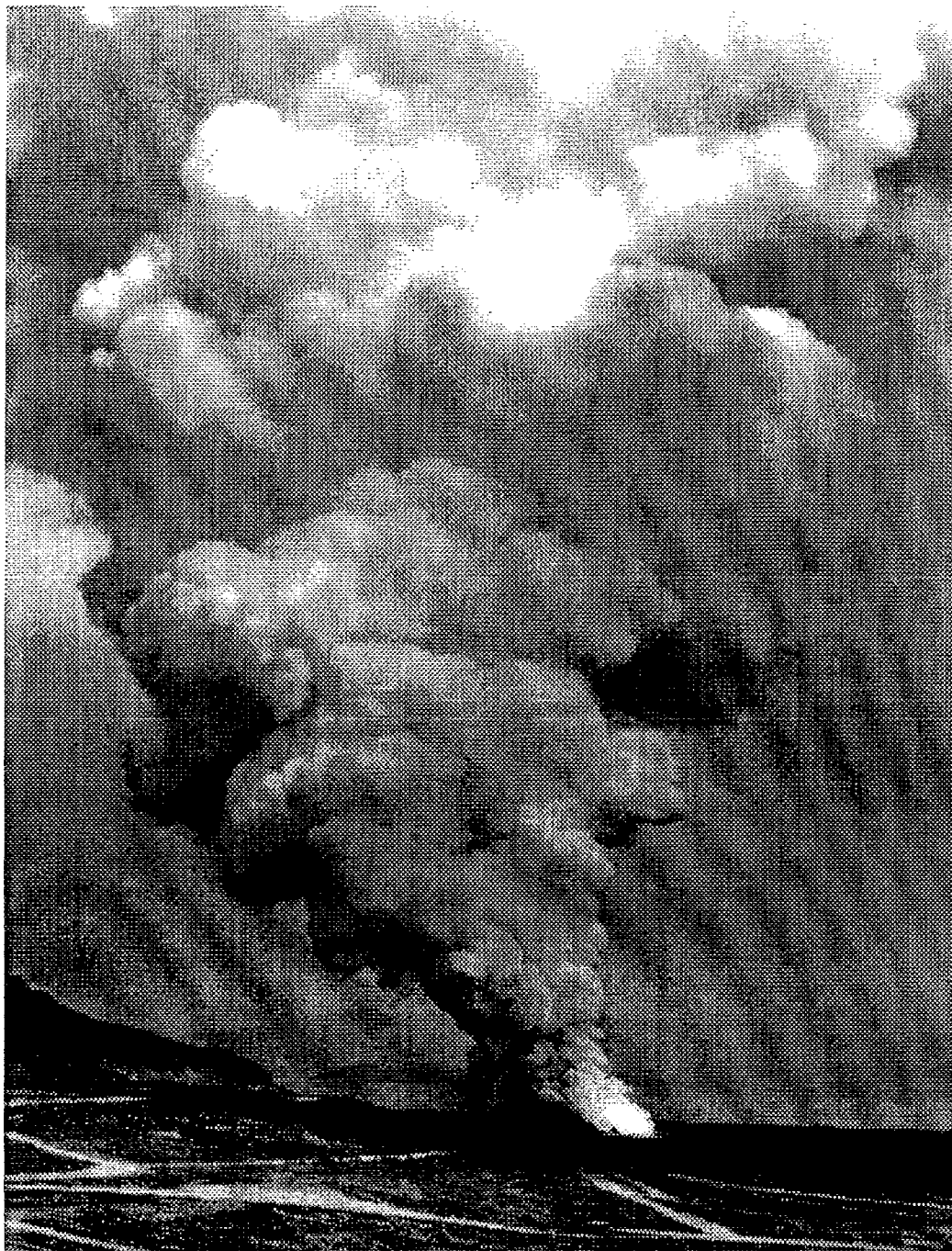
Ammonium Perchlorate Treatment Technology Development

***James A. Hurley
AFRL/MLQE
Tyndall AFB, FL***



***Ammonium Perchlorate - A National Technical Asset
Integral to Strategic Defense Systems - ICBM, SLBM, NRO***





Peace Keeper 1st Stage (98,000 lb)

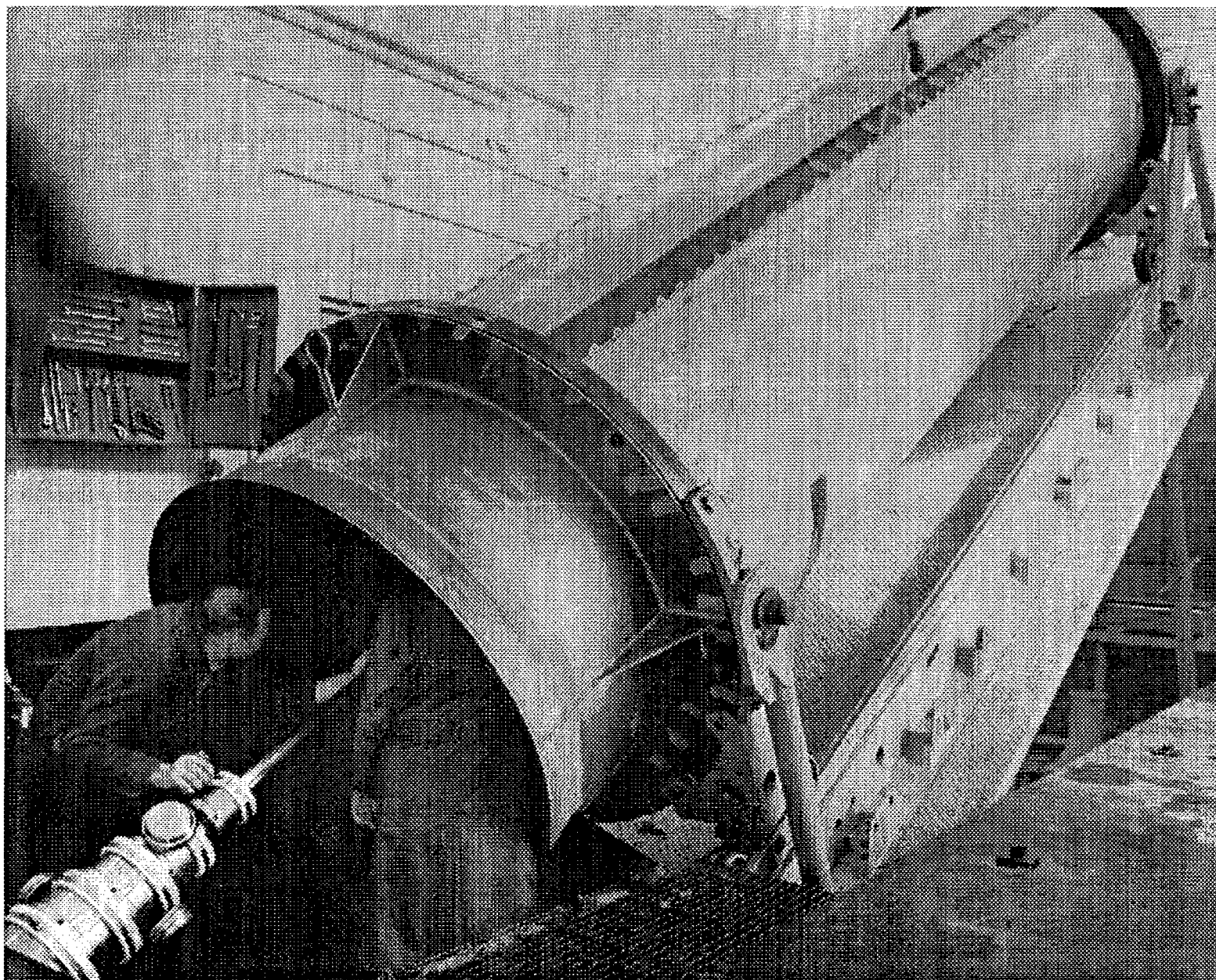
Requirement

- **Increased Demand for Open-Burn/
Open-Detonation (OB/OD) Facilities
with Large-Rocket Motor Capacity.**
 - **START II**
 - **Nunn-Lugar**
 - **Non-Proliferation Treaty**
 - **Multi-National Force Reduction Treaty**

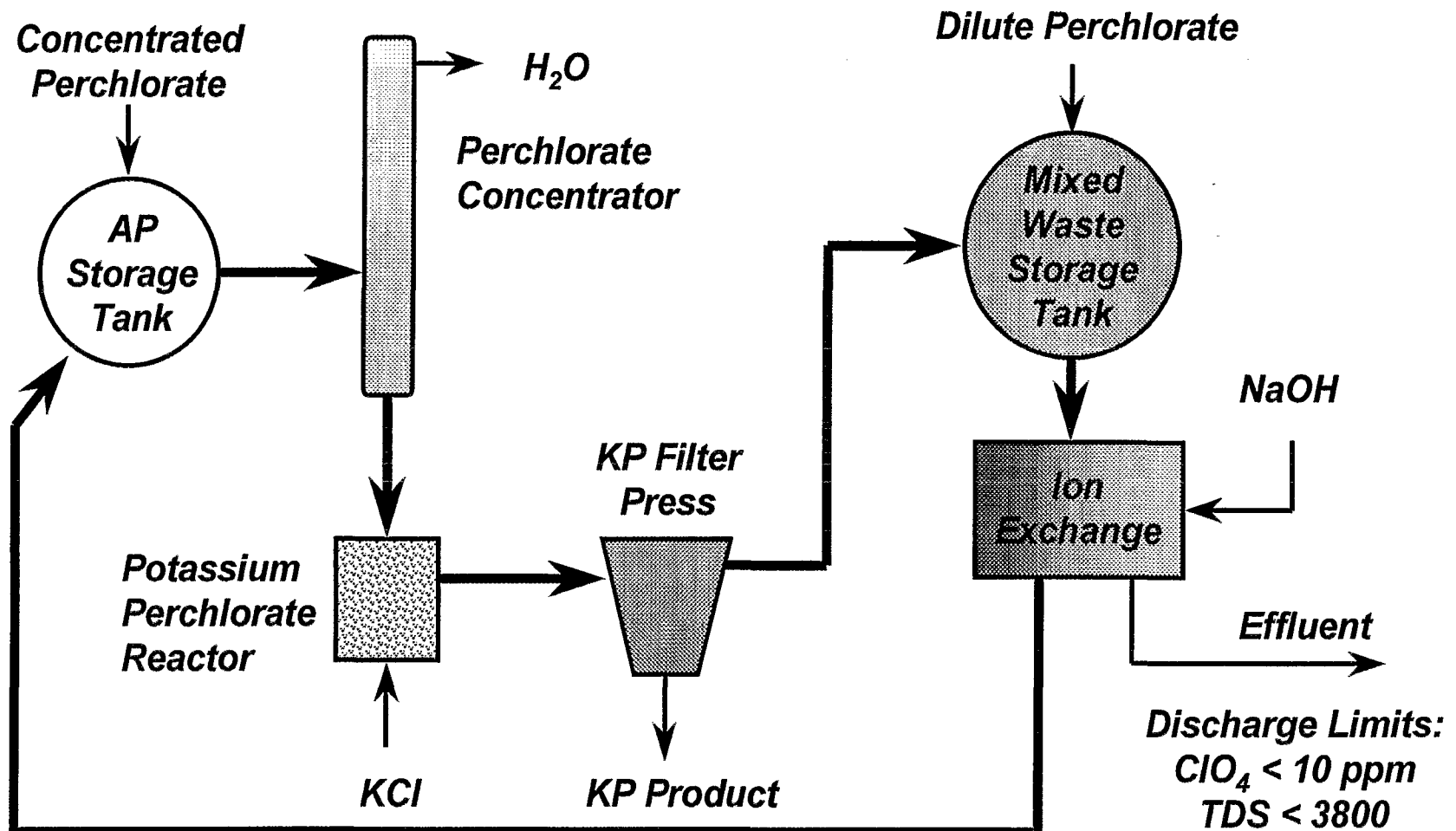
- **Decreased Availability of OB/OD
Facilities.**
 - **Clean Air Act Amendment - 1990
(CAAA)**
 - **Base Realignment and Closure
(BRAC)**

- **Statement of Operational Need
(SON 003-90)**
 - **Joint Logistics Commanders**
 - **Gen McDonald- AFLC/CC**

High-Pressure Water Washout of Solid Propellant

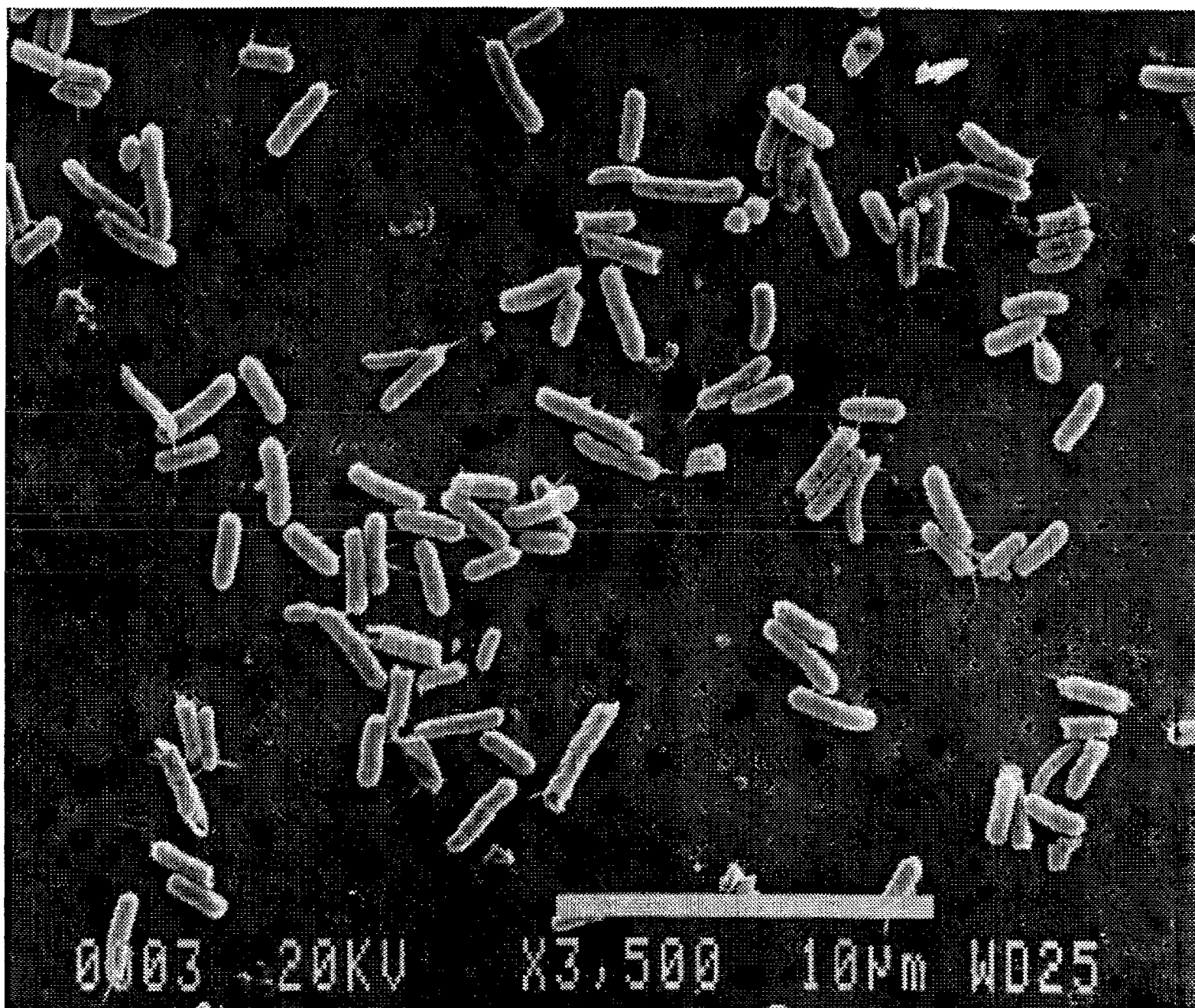


Perchlorate Recovery Process

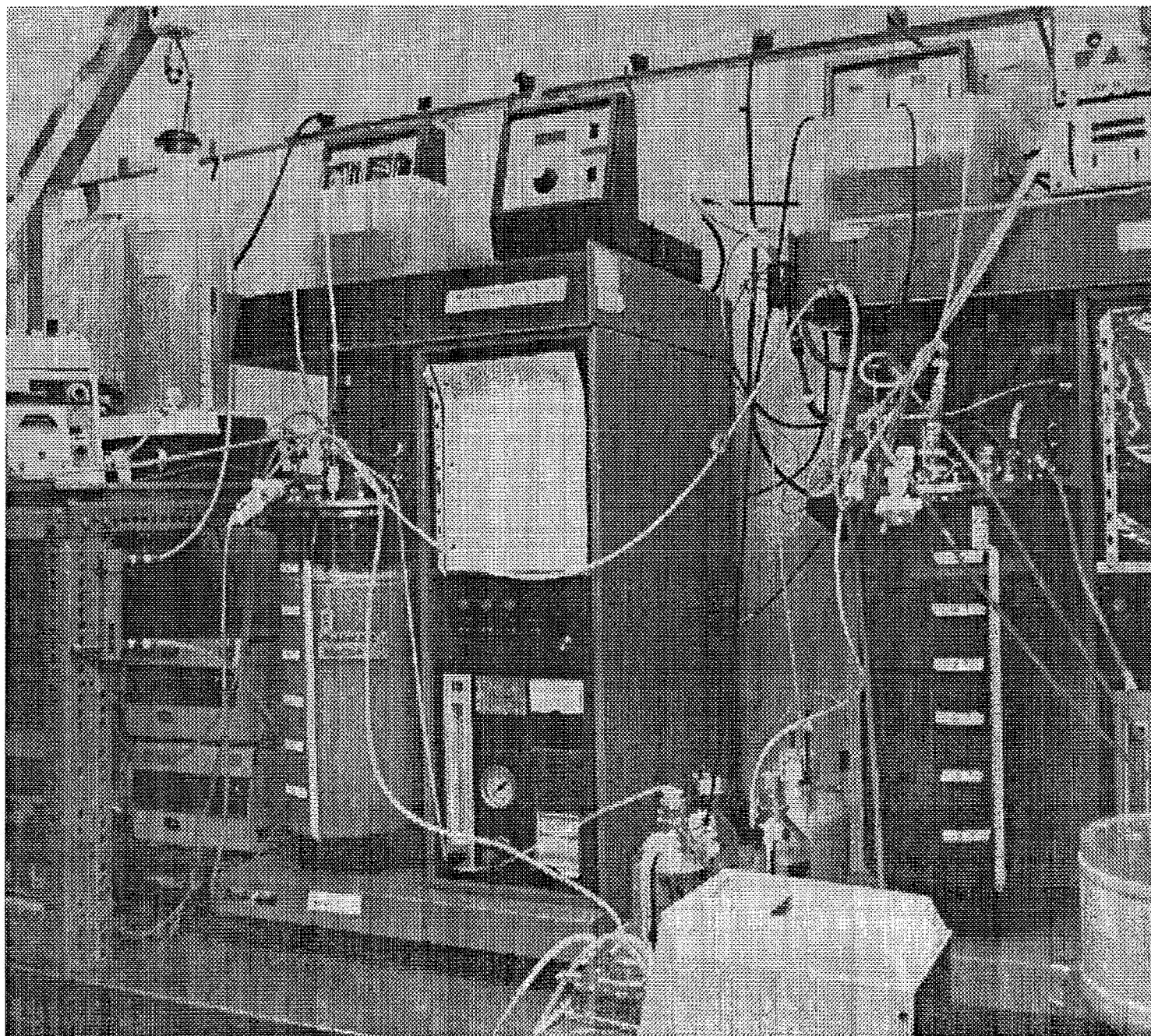


*Higher ClO₄ and TDS increases Ion Exchange Column Regenerations,
More Regenerations Increase Total Dissolved Solids (TDS)*

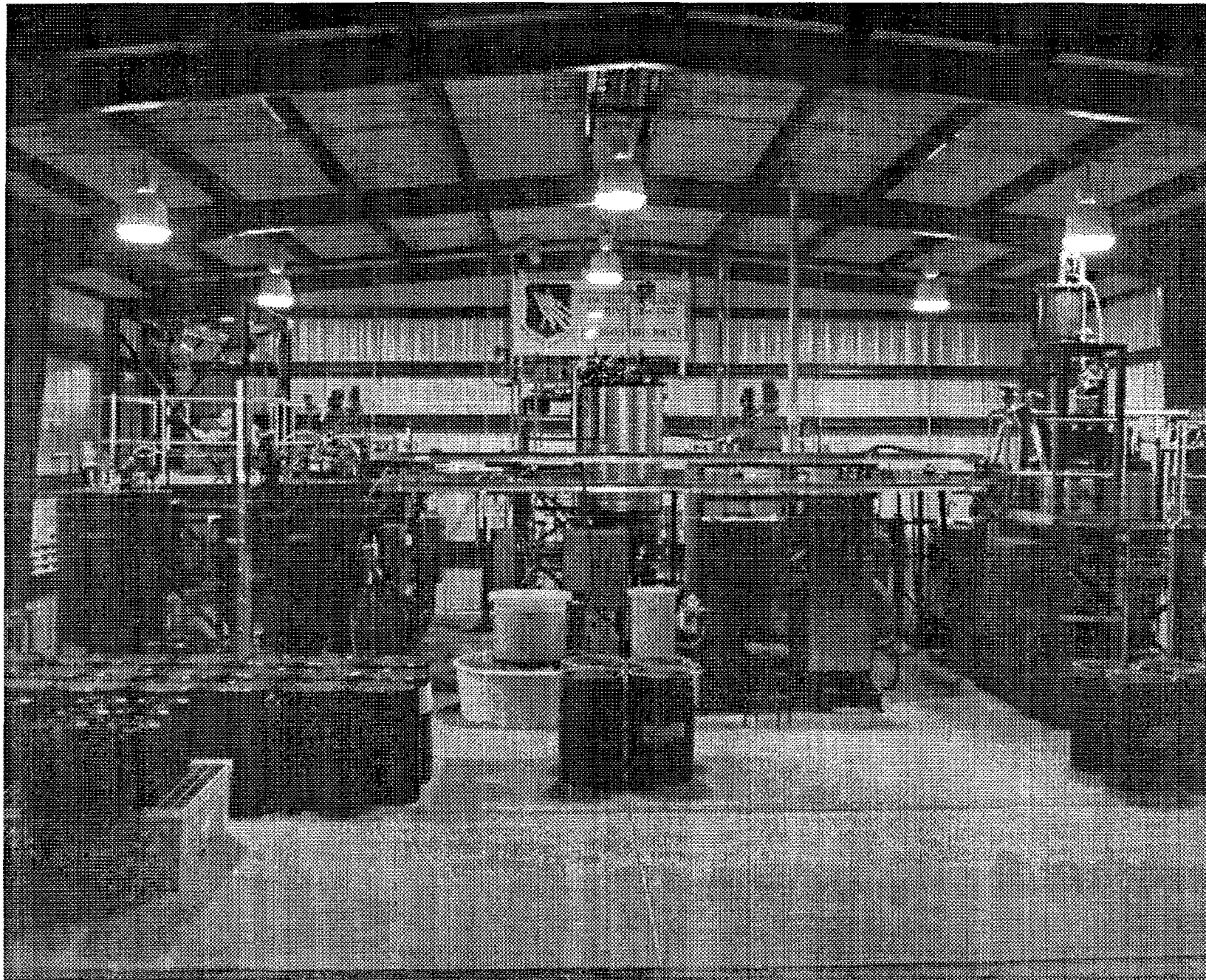
Wolinella succinogenes HAP-1



Bench-Scale Reactor System

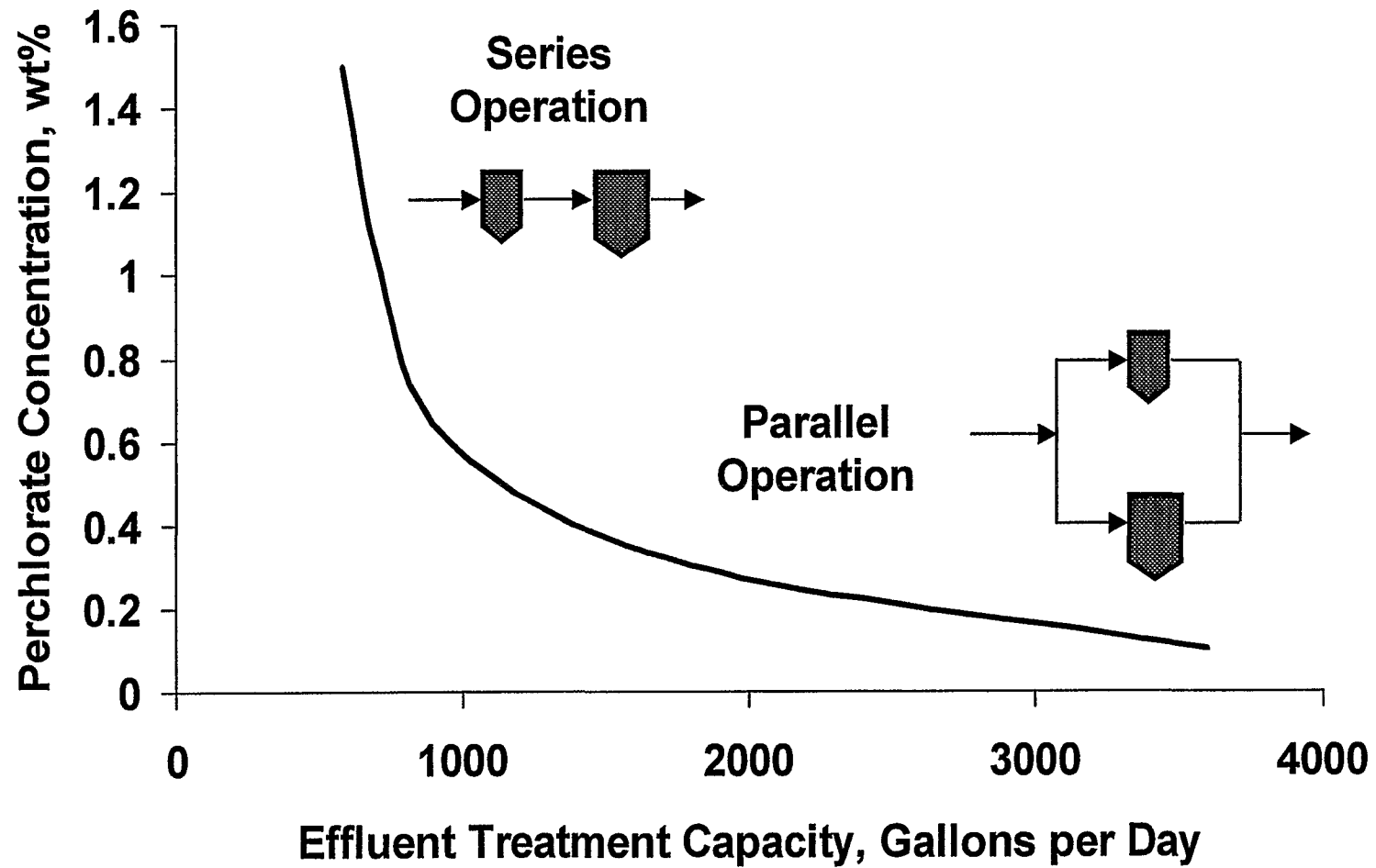


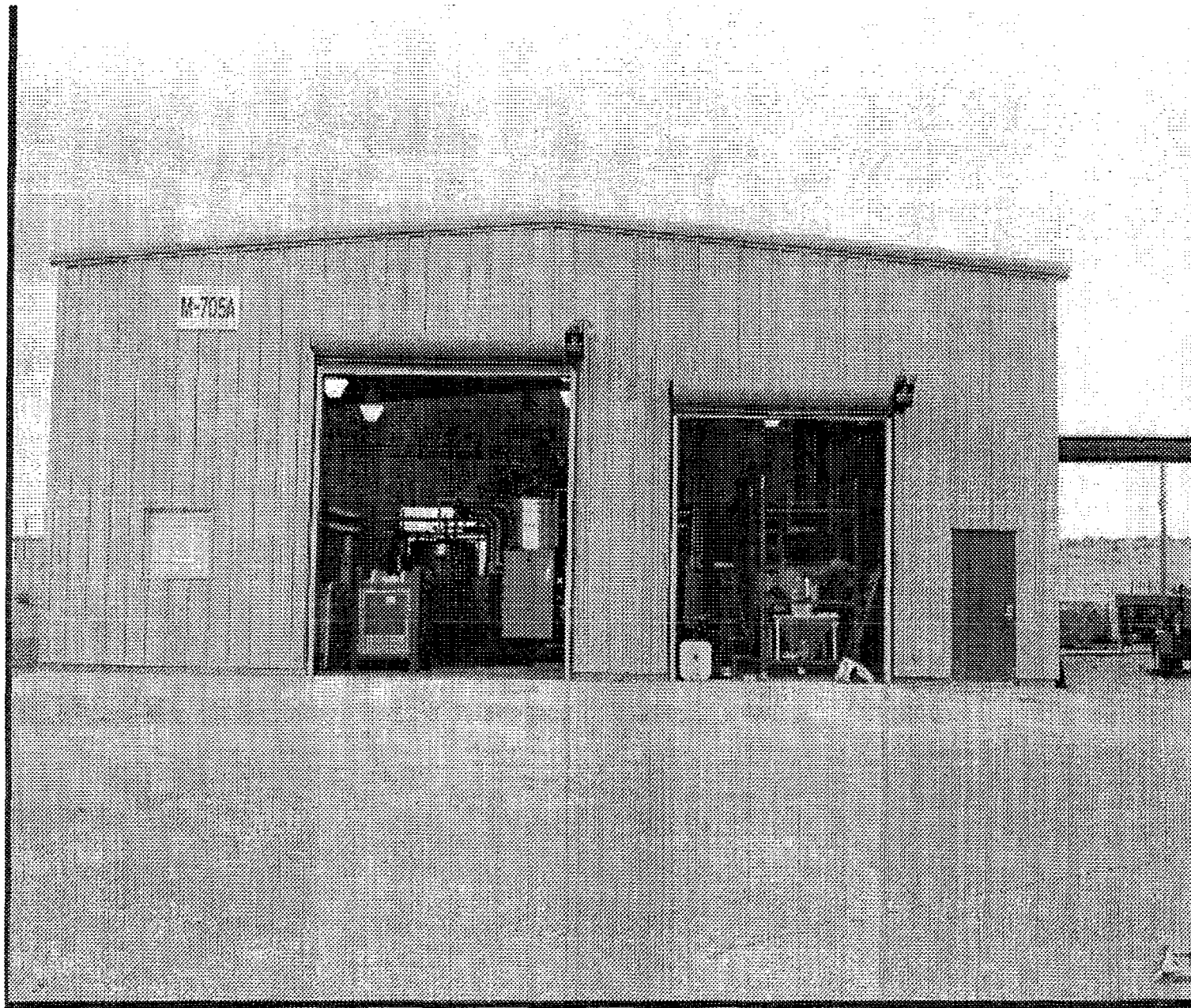
Production-Scale AP Reactor System



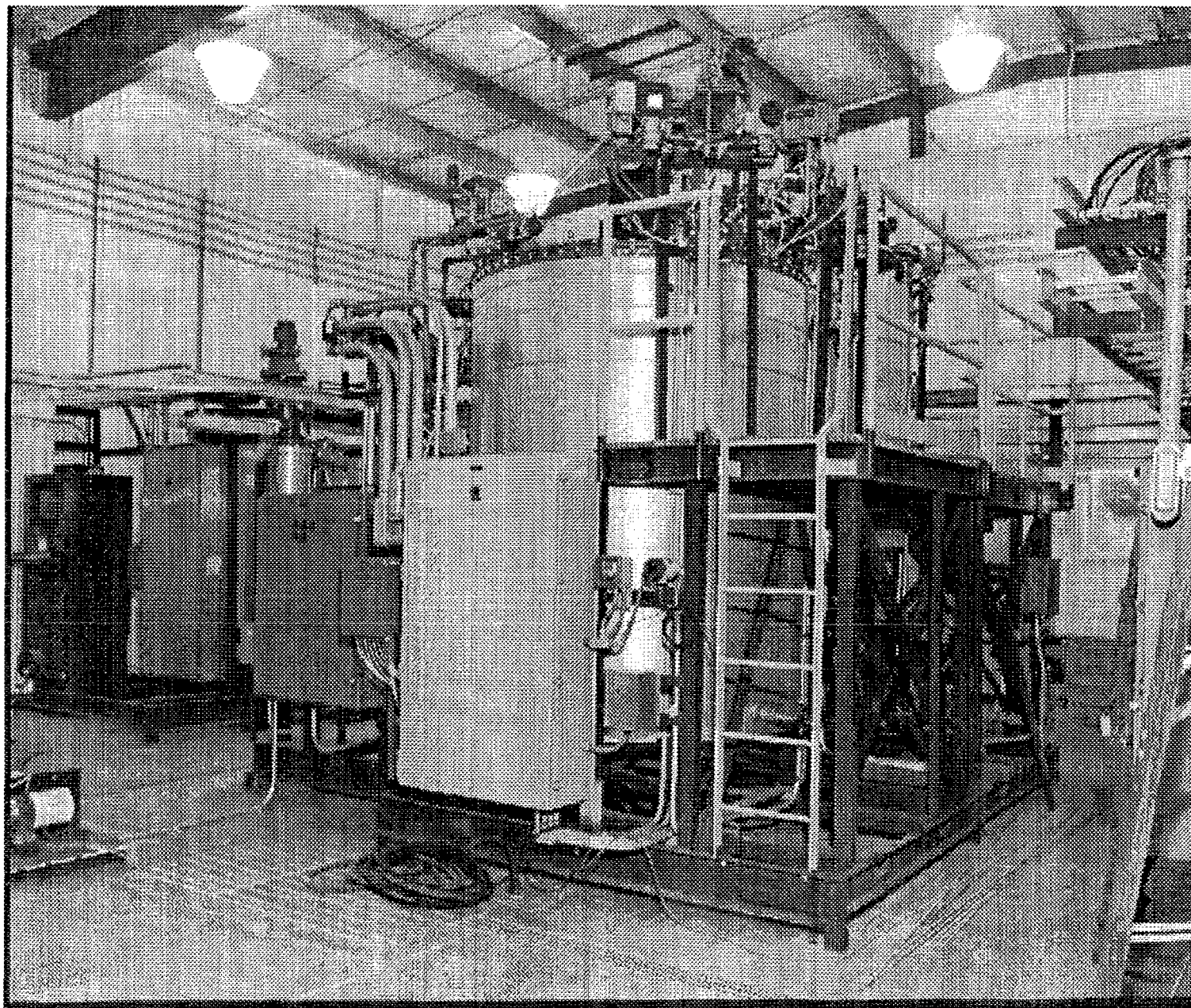


Effect of Perchlorate Concentration on Capacity



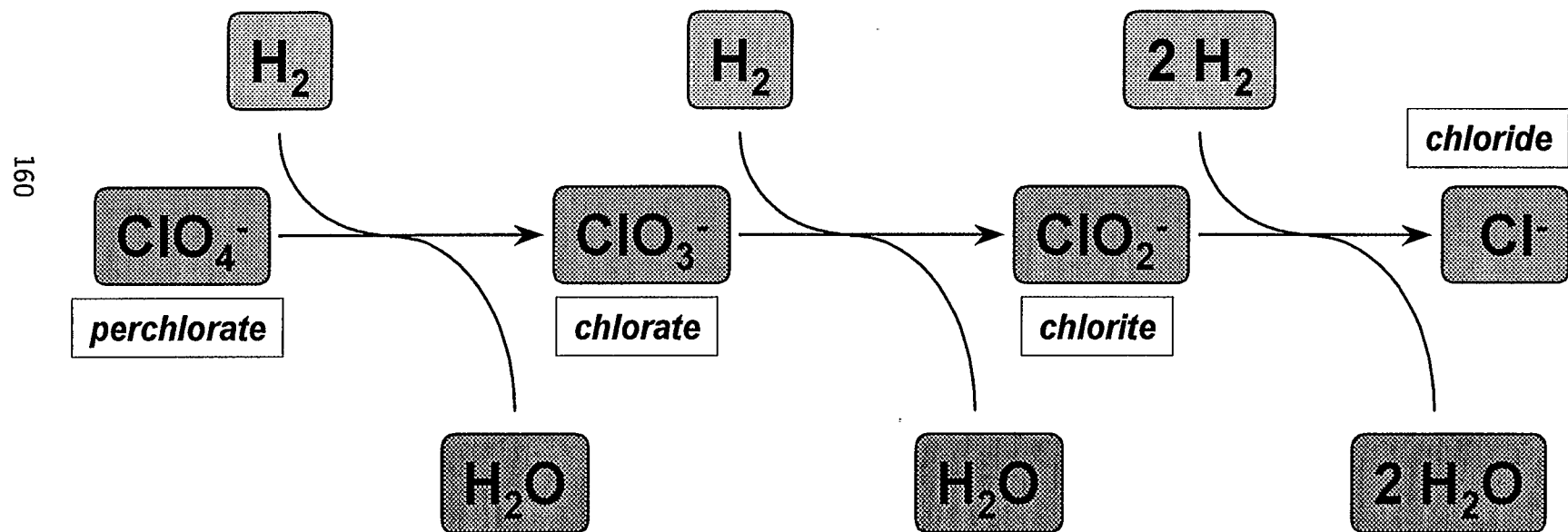


Building at Thiokol Housing the Ammonium Perchlorate Bioreactor System

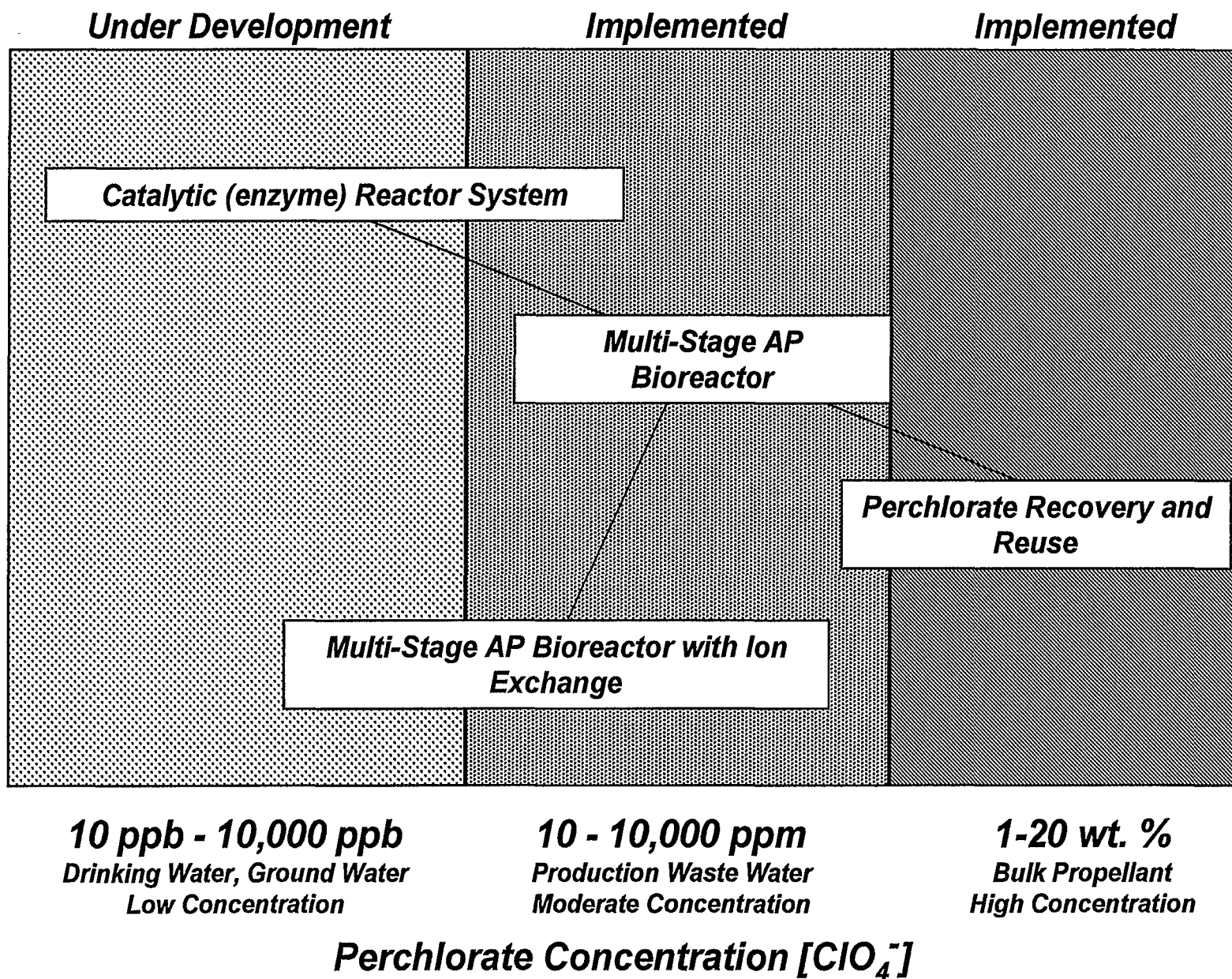


Primary and Secondary Ammonium Perchlorate Reactors

**Metabolic Pathway for Energy Production in
Wolinella succinogenes HAP1**



AP Treatment Technology vs Process Requirement



Low-Concentration AP, High-Volume Wastewater Treatment

Two Approaches

- ❶ ***New (or Improved) Unit Operations Enabling Utilization of
Demonstrated Moderate-Concentration AP Water Treatment***
 - ♦ ***Reverse Osmosis***
 - ***Limited Capacity***
 - ***Requires Effluent Reconditioning***
 - ♦ ***Capacitive Deionization***
 - ***Small Electrochemical Driving Force Limits Capacity***
 - ***Requires Effluent Reconditioning***
 - ♦ ***Ion Exchange***
 - ***Resin Regeneration Very Difficult***
 - ***Efficacy Uncertain at ppb Concentration Level***
 - ***Selectivity Difficult***
 - ***May Require Effluent Reconditioning***

***Low-Concentration AP, High-Volume
Wastewater Treatment (cont.)***

② *New Process for Treating Low-Concentration AP Water Directly*

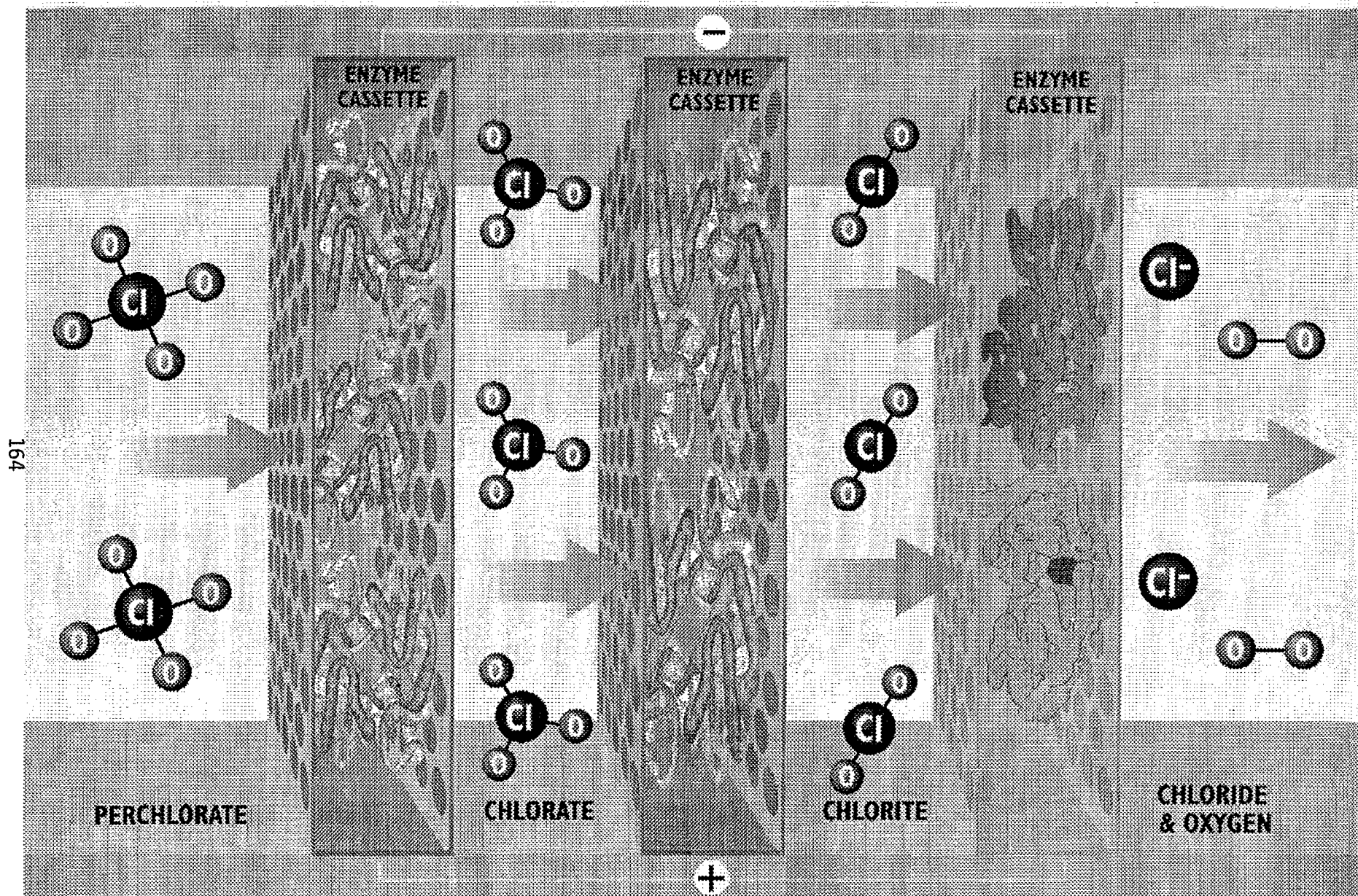
♦ *Conventional Catalytic Reactor System*

- *Non-Selective*
- *Mass-Transfer Limited*
- *Unknown Kinetics, Unknown Efficacy*

♦ *Enzyme Catalytic Reactor System*

- *Anion Specific Selectivity*
- *High Capacity*
- *Wide Application Range*
- *Affect of Other Contaminants Unknown*
- *Requires Multi-Disciplinary Effort*
- *System Sustainability Uncertain*

IMMOBILIZED ENZYME REACTOR



Air Force Benefit

- ***This research and engineering effort has already reduced Air Force weapon system operational cost as well as ensured continued system sustainability.***
- ***The technology developed under this program has wide application in addressing the ever increasing operational constraints and rising costs of materials management at weapon system manufacturing and maintenance facilities.***
- ***Technology insertion (i.e., cost reduction) opportunities are made possible by the continued participation of MLQ in reactor system development for managing Air Force unique materials throughout the weapon system life-cycle.***

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TREATMENT OF LOW CONCENTRATIONS OF PERCHLORATE, STATUS AND ONGOING RESEARCH

Frank J. Blaha, P.E.
AWWA Research Foundation
June 4, 1998

ORGANIZATIONAL BACKGROUND

The American Water Works Association Research Foundation (AWWARF) was created as a related but separate organization from the American Water Works Association (AWWA) in order to pursue drinking water research. The process used by AWWARF to conduct research has a number of means to ensure the scientific validity of the results and the scientific integrity of the research process. Further, the research project results are published by AWWARF for consideration and use by the drinking water community. There are three main AWWARF processes by which research projects are identified for funding, the Research Advisory Council (RAC) process, the unsolicited process, and the tailored collaborative process.

The RAC consists of a group of about 23 experts in drinking water issues. This group meets annually to identify research projects for approximately 70 percent of the AWWARF budget. These projects are identified based on suggestions made to AWWARF as well as an analysis of research needs and research gaps by the RAC. The RAC recommends projects for funding that exceed the available RAC funding budget by approximately 50 percent. The RAC itself is divided into six different subgroups with different technical focus areas. Each of these different subgroups consider the suggested projects and the research gaps in their technical area. The recommended projects from each subgroup are combined and forwarded to the AWWARF Board of Trustees for selection of those that will move forward to the solicitation stage. The projects identified for funding by the RAC and the Board are described in Requests for Proposals (RFP) and advertised for competitive procurement.

Approximately 15 percent of the annual AWWARF budget is allocated to unsolicited research projects. Proposals for these types of projects can be prepared and submitted by any interested parties. Although there are proposal structure and content guidelines, and a proposal due date of April first, there are only general guidelines on the types of projects that are suitable for the unsolicited process. The unsolicited process has been focused on projects that are basic research oriented and should provide a basis and foundation for more applied research projects. The Unsolicited Proposal Research Council is a group of approximately 12 experts in drinking water that meets to evaluate and recommend projects for funding from the unsolicited proposals received. This council also recommends an excess of projects for funding. These recommended projects are then forwarded to the AWWARF Board of Trustees for final decision of those projects that will move forward to the funded research stage.

Another 15 percent of the annual budget is allocated to tailored collaborative projects. These are projects that are of particular interest to a utility or group of utilities, but should also be of interest to a broader portion of the drinking water community. Proposals for these projects are identified by interested parties and submitted to AWWARF for consideration. The Tailored Collaboration Review Council meets to consider the proposals from the perspective of the technical work proposed, the applicability of that technical work, as well as the requested budget. These projects are partly funded by the participants and partly funded by AWWARF. AWWARF will provide up to one dollar in matching funds for each dollar that is contributed by the participants.

Issue Groups are also conducted by AWWARF to comprehensively address a high priority technical area. Issue Groups normally identify a multiyear research plan to address the issue. The Issue Group projects are funded from a percentage of the funding in one of the six general technical categories by which the RAC is

divided. The final project recommendations from the Issue Groups are forwarded to the Board for final approval. The approved projects normally are then advertised for competitive procurement.

AWWARF has also entered into a number of partnerships and research agreements with organizations such as the Environmental Protection Agency (EPA) and the Bureau of Reclamation. Although there is no set standard for how these partnerships are structured, there is normally a joint committee of experts created that have both technical and budgetary responsibilities. These partnerships are often funded by the partnering organizations, with AWWARF providing up to 50 percent of the funding. Normally a set of information is created addressing the issue and relevant projects so that information gaps can be identified. Identified and funded research projects are normally advertised for competitive procurement through an RFP process. At this time AWWARF has six separate ongoing research agreements with EPA totaling approximately \$10,550,000 in committed research. Periodic progress reports to EPA describing the ongoing project are normally required for these agreements.

Regardless of the process used to identify an AWWARF project for funding, during the project period the investigator makes periodic progress reports to AWWARF and the Project Advisory Committee (PAC). The PAC is a volunteer group of technical experts that provides ongoing peer review of the project from drafting of the RFP through the final report. For those projects that go through an RFP and competitive procurement process, the PAC identifies the winning proposal, if any. The PAC is identified by AWWARF for the technical expertise of the individuals as well as for their lack of a conflict of interest. Although the size of a PAC varies, they normally consist of three individuals. Comments from the PAC are offered to the investigator throughout the project period. Should serious problems with the scientific integrity of the research project be identified, the PAC has the authority to end the project.

PERCHLORATE BACKGROUND

California water utilities first brought the perchlorate issue to AWWARF's attention in June of 1997. A new analytical procedure developed by the California Department of Health Services (CDHS) had reduced the detection limit for perchlorate from 0.400 milligrams per liter (mg/l) to 0.004 mg/l. This new method was first developed in March 1997. Based on United States Environmental Protection Agency (EPA) work reviewing the toxicology of perchlorate, which recommended reference dose levels of perchlorate in drinking water from 0.004 – 0.018 mg/l, CDHS adopted a provisional action level of 0.018 mg/l for perchlorate in drinking water. Using the new method, the CDHS had, by June 1997, sampled 232 ground water wells and found perchlorate in 69 of them at various concentrations. Twenty of these wells contained perchlorate above the State's provisional action level of 0.018 mg/l. A number of California water utilities were concerned that a comprehensive research program be created to address perchlorate contamination. Based on this information, the AWWARF Board of Trustees approved limited AWWARF involvement in further defining the problem and related research needs.

By late summer of 1997 the understanding of environmental perchlorate contamination had advanced considerably, but there appeared to be a major knowledge gap in treating low concentrations of perchlorate contamination. Most perchlorate-related treatment research to that time had concentrated on water containing 8 to 9 mg/l, or higher concentrations, of perchlorate. Region IX of the EPA, the CDHS, the Air Force, and others had been reviewing the literature and searching for perchlorate treatment methods effective at the levels being found in drinking water supplies. Their consensus at that time was that there was no proven removal process available at the low concentrations being found in drinking water. Aerojet, a significant user of perchlorate, was known to be developing a proprietary bioremediation system for high concentrations of perchlorate. The Air Force, in cooperation with the industry, was also known to be working on biological treatment processes for high concentrations of perchlorate. Limited experience using relatively conventional water treatment practices such as granular activated carbon (GAC), ion exchange, air stripping, and advanced oxidation were found to have limited or no effect in treating low concentrations of perchlorate. Reverse osmosis was found effective but the ratio of treated water to rejected water was

unknown. The issue of perchlorate residual disposal was a serious concern in some of the treatment methods.

ISSUE GROUP MEETING

The combination of these unresolved issues, especially the lack of a treatment technology for low concentrations of perchlorate contamination, attracted congressional interest, particularly in the California delegation. Through efforts led by Rep. Jerry Lewis (R., Calif.) the House-Senate Conference Committee on Appropriations on September 30 earmarked \$2,000,000 for the East Valley Water District, San Bernardino, California, for research into treatment methods for perchlorate. In anticipation of this funding, the East Valley Water District, in cooperation with four other water suppliers, (Main San Gabriel Basin Watermaster, Metropolitan Water District of Southern California, San Bernardino Valley Municipal Water District, and the Southern Nevada Water Authority) had sponsored a research planning workshop which they requested AWWARF to organize and manage. Based on this possible funding, AWWARF agreed and convened an expert workgroup of 27 participants that included CDHS, EPA Region IX, university professors and researchers, Aerojet and the Air Force, consultants and other research experts, as well as technical representatives of the sponsoring water utilities. Using a modification of the planning process for other AWWARF research issue groups, AWWARF conducted the perchlorate issue group in Ontario, California, September 30-October 2, 1997. The task for this issue group was development of a multiyear research plan to address the perchlorate problem.

Preparatory materials had been assembled by AWWARF staff and distributed to the issue group participants prior to the meeting. These materials addressed the then current status and understanding of the perchlorate problem. When convened the issue group discussed the overall status of the problem and, based on already available information, focused their efforts on treatment and analytical methodology research needs. Briefly explained, the issue group meeting consisted of the following elements:

- Group introductions; background information on workshop sponsorship, purposes, and objectives; ground rules.
- A series of seven brief presentations:
 - ◊ Summary of current health effects information by Major Dan Rogers, U.S. Air Force
 - ◊ Overview of occurrence studies, recent and planned, by Frank Blaha, AWWARF
 - ◊ New analytical method and related issues by Joe Donnelly, EPA National Exposure Research Laboratory
 - ◊ Aerojet bioremediation method by Mike Girard, Aerojet
 - ◊ Air Force bioremediation research by Jim Hurley, Tyndall Air Force Base/Armstrong Laboratory
 - ◊ Lawrence-Livermore National Laboratory research by Ravi Upadhye, Lawrence Livermore National Laboratory
 - ◊ Overview of prospects for other treatment technologies by Kevin Mayer, EPA
- An eighth briefing was added on a just-completed survey of treatment methods by consultants working with Aerojet on the San Gabriel Superfund site. Perchlorates as well as other contaminants impact this site which constitutes some of the source water for the San Gabriel area in California. John Catts of Harding Lawson Associates provided this briefing.
- The large group was then split into three concurrent smaller workgroups--Analytical Methods and Occurrence, Utility and Regulatory Requirements, and Treatment Options. Each of these individual groups identified research needs that were then presented to the whole group for discussion and refinement. The utility group also listed operational requirements for proposed treatment processes.
- Based on the comments of the large group, the smaller workgroups met again to draft detailed project descriptions.
- Seventeen project descriptions were reproduced for review by all participants. These project descriptions included a description of the anticipated project scope and a suggested budget. Suggested

changes were discussed in a large group session that concluded with agreement on all projects to be recommended by the workshop. Two education/information projects, as opposed to research projects, were identified for reference to AWWA for action.

- The participants then developed a matrix in which each project was assigned a priority and a start-up year.

The Utility and Regulatory Requirements workgroup had as one of its assignments the identification of practical operational criteria for perchlorate treatment methods. The list they generated was accepted by the other participants as valid, if ideal, criteria. The workgroup's report included:

- Effective treatment methods should be sought to reduce perchlorate contamination of drinking water to 0.004 mg/l.
- Disposal of any residuals generated by a perchlorate treatment technology should be considered as a key treatment technology variable.
- Perchlorate contamination is already impacting many water utilities. Therefore, research on perchlorate treatment should consider and address real water matrices that can consist of a number of different contaminants that impact treatment. The interplay of various common, or expected, contaminants in perchlorate-contaminated water must be addressed.

The issue group participants also agreed to some other generally applicable concepts and criteria for treatment related research projects. These include:

- A variety of treatment methods will be needed to address a variety of source water qualities.
- The treatment projects should address concentrations of perchlorate being experienced in utility source waters.
- The treatment projects should be managed in such a way as to minimize the amount of time needed to develop pilot-scale treatment data.
- The treatment methods should consider the interrelationship of treatment methods and other water utility issues.

Table 1 lists the research topics developed by the issue group, displays the priority ranking assigned to each, the estimated funding required (in thousands), and the recommended start-up year. It should be noted that due to the urgency of the perchlorate issue, some of the projects identified by the issue group were large multi-phased projects covering bench-scale to pilot-scale activities. This approach was taken so that treatment methods showing promise could be taken from the conceptual stage all the way to full-scale application in as little time as possible. Some of the projects were identified to have two simultaneous awards to different researchers. These simultaneous awards were identified due to either the high likelihood of success in developing a treatment process, or due to the importance of the consideration in the overall perchlorate treatment program.

REGULATORY FRAMEWORK/CONCERNS OF UTILITIES

Throughout much of this century the typical water disinfectant has been chlorine. Some of the microorganisms found in drinking water are pathogenic, meaning they can cause illness and disease, and it has been an overriding concern to remove or inactivate such organisms from drinking water. The increasing use of chlorine and other disinfectants throughout this century has resulted in considerably safer drinking water and a much reduced incidence of water-borne illness (Pontius, 1998).

However, in 1974 the EPA and others discovered that chlorination of drinking water could also cause the creation of trihalomethanes. These trihalomethanes, which are considered carcinogenic, are formed from

the reaction of chlorine with natural organic matter (NOM) (Pontius, 1998). NOM is found in various levels in all natural waters.

Since the 1970s considerable additional research has been conducted on the reactions of disinfectants with NOM and other compounds. At this time a whole series of disinfectant by-products (DBPs) have been identified. DBPs have been identified that are associated with the use of any disinfectant. The currently identified DBPs include inorganic compounds, trihalomethanes, haloacetic acids, cyanogen halides, haloacetonitriles, haloaldehydes, halophenols, chloral hydrate, and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone. Similarly, much more work has been devoted to the characterization of NOM in drinking water. Work has been done to isolate and better understand the humic fraction, fulvic fraction, polar fraction, nonpolar fraction, and DBP formation potential of NOM (Pontius, 1998). These different fractions of NOM have been studied from the perspective of their behavior in generation of DBPs, as well as the ease of removal of these various fractions from water.

The first regulation of DBPs was promulgated in 1979 when the level of total trihalomethanes in drinking water was set at 0.100 mg/l. It was a policy assumption of this regulation that no safe level exists for human exposure to carcinogens, and that the concentrations of these compounds in drinking water should be reduced to the extent feasible. New DBP regulations were proposed by EPA in 1994, with finalized rules expected in November 1998. It is expected that levels for DBPs will be set at 0.080 mg/l for total trihalomethanes, 0.060 mg/l for five haloacetic acids, 0.010 mg/l for bromate, and 1.0 mg/l for chlorite. EPA has as a basic consideration in the proposed DBP rule that there be no reduction in total effective disinfection at water utilities; the protection of the public from pathogens in drinking water continues to be a primary concern (Pontius, 1998).

These pathogen and DBP-related considerations are of importance to the perchlorate research program identified at the AWWARF issue group. For instance, there are developed biological treatment systems for high concentrations of perchlorate in water. It seems highly likely that these treatment methods can be modified and applied to low concentrations of perchlorate in water. However, the developed biological treatment systems require the addition of a carbon source to the water in order to allow the biological conversion of perchlorate to chloride.

There are a number of concerns related to the addition of a carbon source to a water to be treated for drinking water purposes. These considerations include:

- A possible increase in the DBP formation or DBP formation potential of the drinking water
- Carry-over of microorganisms from the treatment process into the drinking water
- Increased NOM in the finished water and biological regrowth in the distribution system
- Changed water quality and related inorganic reactions in the distribution system
- Taste and odor concerns
- Increased disinfectant demand

The regulatory acceptance of a biological treatment process for perchlorate in drinking water is likely to prove costly and time-consuming, thus negatively impacting the full-scale application of this type of treatment process to drinking water. Clearly there needs to be a variety of treatment options for perchlorate removal from drinking water.

A proposed treatment project that deserves additional discussion is the ozone/GAC project. This project is not attempting oxidation of the perchlorate with ozone, it instead relies on ozone modification of the NOM already present in the water. This modified NOM can serve as a substrate for biological activity in the carbon column in addition to other possible reactions associated with the activated carbon. This type of advanced oxidation treatment process is relatively accepted in the drinking water field. It is thus more likely of quick regulatory approval than some biological treatment processes. Another consideration in application of perchlorate treatment methods is the difficulty of implementation. Many more utilities have GAC treatment operations in place than ion exchange treatment. Retrofitting a plant that has an existing

GAC process to allow for advanced oxidation will likely prove easier and less costly than construction of a new treatment process at that same utility. These types of considerations were built into the proposed treatment program.

CURRENT STATUS OF THE AWWARF PERCHLORATE RESEARCH PROGRAM

Seven RFPs were advertised by AWWARF for perchlorate projects in March of 1998. Two of these seven projects were analytically related and received no proposals. Proposals were received for all of the five treatment-related projects. These treatment projects all have a phased scope. Phase I is to be laboratory and bench scale development of the potential treatment process. Those projects that appear likely of success in Phase I will move into Phase II which is pilot scale testing. It is a requirement of the RFPs, as it is of the Congressional earmark, that Phase II activities address the Crafton-Redlands plume. The Crafton-Redlands plume of contaminated groundwater is found in the Redlands area of California.

The original schedule was to identify winning proposals no later than mid-June of 1998. Contracts should be completed 4 to 8 weeks after selection of the winning proposals. Contracted treatment work should start by August or September of 1998. However, this schedule is contingent upon the allocated moneys being released from EPA to the East Valley Water District.

REFERENCES

Pontius, Frederick W., 1998, *Small Systems to Tackle Disinfection By-Products*, Journal American Water Works Association, Volume 90, Number 4, Pages 14, 176.

TABLE 1
Proposed Research Projects Developed by the Perchlorate Issue Group September 30-October 2, 1997

Group	Project Title	Priority Ranking	1998	1999	2000	2001
Treatment	Application of Bioreactor Systems to Low-concentration Perchlorate Contaminated Water	1	688		320	
Treatment	Treatability of Perchlorate-Containing Waters by Reverse Osmosis and Nanofiltration	1	312		513	
Treatment	The Treatability of Perchlorate in Groundwater Using Ion Exchange Technology	1	312		513	
Analytical Methods	Survey the Performance of the California DHS (Ion Chromatography) Analytical Protocol	1	94			
Analytical Methods	Short Term Perchlorate Laboratory Issues	1	125			
Treatment	Removal of Perchlorate and Bromate in Conventional Ozone/GAC Systems	2	188	577		
Treatment	Investigation of Methods for Perchlorate Destruction in Aqueous Waste Streams	2	250		577	
Treatment	Assessment of Enzyme Based Reactor Systems on Perchlorate Reduction	3		385		1,090
Treatment	Literature/Expert Panel Review for Effective In-situ Treatment Technologies for Treatment of Perchlorate in Soil and Groundwater	3	63			
Treatment	Demonstration of Electrodialysis and Electrodialysis Reversal as a Control Technology for Perchlorate-Containing Waters	3		577		
Treatment	Investigation of Innovative Technologies for Perchlorate Removal from Drinking Water Sources	3		385	577	
Analytical Methods	Development of an Alternative Analytical Method for Measuring Perchlorate Ion at the 4 PPB Level	3			160	
Analytical Methods	Inter-Laboratory Study for the Performance Evaluation of the Cal-DHS Method: Determination of Perchlorate by IC	3		128		
Occurrence	Fate and Transport of Perchlorate in Drinking Water Sources	3	250	256		
Health Effects	Assess the Current Regional Health Effects Associated with Perchlorate in Ground and Surface Water Supplies	3		513	577	
	TOTAL		2,282	2,821	3,237	1,090

1 - Higher Priority Projects
2 - Medium Priority Projects
3 - Lower Priority Projects

NOTES 1 Funding is shown in thousands of dollars
2 Only the higher and medium priority projects identified for 1998 were funded.

Future Perchlorate Treatment Studies

William J. Blanton, P.E.

AWWA Research Foundation

June 4, 1998



Organizational Background

- American Water Works Association Research Foundation
- In existence since 1965
- Most active since about 1984
- AWWARF Charter
- Related to but separate from AWWA



Organizational Background, *continued*

- AWWA created in 1881
- AWWA Charter
- Perchlorate brought to Foundation's attention in June 1997
- California water utilities concerned about impact
- AWWAF BOT approved limited involvement in June 1997



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AWWARF Process

- Three main research project identification methods
 - ◆ Research Advisory Council for solicited proposals—70 percent
 - ◆ Unsolicited proposals process—15 percent
 - ◆ Tailored Collaboration process—15 percent
- Partnerships—USEPA
- Research agreements—USEPA
- Issue groups



AWWARF PROCESS, *continued*

- **Research Advisory Council meeting —
solved projects**
 - ◆ **Twenty-three utility, water quality, water
treatment, consultant, supplier experts**
 - ◆ **Two and one-half day meeting to address
needed research gaps**
 - ◆ **Take suggestions from water community as a
start**



AWWARF Process *continued*

◆ Split into six separate technical groups:

- Microbiology
- Chemicals
- Management
- Infrastructure
- Customer
- Resources and Residuals

- ◆ Recommend greater than 100 percent expected AWWARF solicited budget
- ◆ Requests for proposals
- ◆ Board makes final decision



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AWWARF Process, *continued*

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 - Customer
 - Resources and residuals
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AWWARF Process, continued

- Unsolicited proposal process
 - ◆ Want to address need for basic research on which more applied research can be based
 - ◆ April proposal date, general criteria
 - ◆ Evaluation council of approximately 12 people
 - ◆ Projects selected and recommended to Board at greater than 300 percent expected unsolicited budget
 - ◆ Board makes final decision
 - ◆ Contracts completed



AAWWARE Process *continued*

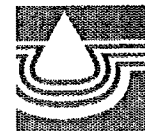
■ **Partnerships—USEPA (M/DBP arsenic)**

- ◆ **Joint committee of experts to identify work**
 - **Technical review committee**
 - **Final decision-making committee**
- ◆ **Jointly funded budget:**
50 percent USEPA, 50 percent RF
- ◆ **Maximum funding level pre-approved by Board**
- ◆ **Prepare notebook on relevant issues and projects**
- ◆ **Identify needed research to address gaps**
- ◆ **Projects then to RFP stages**
- ◆ **Projects split with respect to management:**
USEPA/RF



AWWARF Process, *continued*

- **Current research agreements with USEPA**
 - ◆ Six agreements covering the last six years
 - ◆ Other agreements totally completed
 - ◆ \$10,550,000 total in current agreements
 - ◆ USEPA Project Advisory Committee (PAC) member normally required
 - ◆ Periodic progress reports to USEPA



AWWARF Process, *continued*

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AWWARF Process, continued

■ **Issue groups**

- ◆ **Convene group experts to comprehensively address a high priority technical area**
- ◆ **Possible multiyear plan**
- ◆ **Funded from a percentage of funding in one of six general technical categories**
- ◆ **Final project recommendations to Board for approval**



AWWARF Process, *continued*

- During project period the investigator makes periodic reports of project progress to AWWARF and the Project Advisory Committee (PAC)
- PAC identified for all projects
- PACs are volunteer technical expert reviewers
- The PAC provides ongoing peer review on a project from drafting of the RFP through the final report
- Perchlorate treatment projects will also be peer reviewed by East Valley Water District (EVWD)



Perchlorate Research Program

- Most of 1998 work will be funded from a \$2,000,000 Congressional earmark
- Congressman Jerry Lewis of California was the champion for obtaining this earmark
- Earmark for treatment related research
- Funding to go to EVWD
- EVWD in turn working with AWWARF to manage the research
- Must address the Crafton-Redlands Plume



AWWARF Process, *continued*

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EVWD/AWWA Issue Group Meeting

- Held in anticipation of the Congressional earmark
- Held in fall of 1997, in Ontario, Calif.
- Issue Group: Workshop to Develop a Multi-year Research Plan
- Focused on treatment and analytical methodology research needs
- Funded by
 - ◆ EVWD
 - ◆ Main San Gabriel Basin Watermaster
 - ◆ Metropolitan Water District of Southern California
 - ◆ San Bernardino Valley Municipal Water District
 - ◆ Southern Nevada Water Authority



EVWD/AWWARF

Issue Group Meeting *continued*

■ Twenty-seven participants

- ◆ Stakeholders
- ◆ Experts in potential treatment technologies
- ◆ Experts in analytical issues for perchlorate

■ Breakdown of participants

- ◆ Eight water utility representatives
- ◆ Five from academia
- ◆ Six consultants or other research organizations (LLNL)
- ◆ Three perchlorate users/DO
- ◆ Five regulatory agencies
- ◆ One facilitator with considerable water utility experience
- ◆ Three AWWARF staff members



VWD/AWWA/F

Issue Group Meeting continued

- Addressed status of the problem discussed issues
- Identified relevant research needs
- Broke up into small working groups to define individual projects



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EVWD/AWWA RF

Issue Group Meeting, *continued*

- **Utility and regulatory group conclusions**
 - ◆ Effective treatment methods should be sought to reduce perchlorate in drinking water to 4 ppb
 - ◆ Disposal of residuals from treatment must be considered a key treatment technology variable
 - ◆ Treatment method development should address real water matrices—interplay of various common or expected contaminants must be addressed



Treatment Project Background

- Variety of treatment methods needed to address variety of source water qualities
- Address concentrations in utility source waters
- Treat to less than detection limit/4 ppb
- Minimize time needed to develop treatment methods: need pilot scale data soon
- Consider interrelationship of treatment methods and other water utility issues



Regulatory Framework and Relevant Concerns of Water Utilities

- 1961—Drinking water quality standards set by AWWA
- 1962—USPHS adopts AWWA standards for nation
- 1970s, 1980s—Water industry reactive to USEPA regulations



EVWD/AWWARF

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Regulatory Framework Relevant

Concerns, continued

January 1988 — Jack Hollibaugh,
Executive Director, AWWA:

*“We are going to move forward
with the information at our
disposal and do what we do
best—protect public health.”*



Regulatory Framework/Relevant Concerns, *continued*

- Recent epidemiological study from California: correlation between total trihalomethane (TTHM) concentrations in drinking and miscarriages
- TTHMs are disinfection by-products (DBPs)



Regulatory Framework/Relevant Concerns, *continued*

■ MDDP Rule

- ◆ 1854—Snow (?) on cholera
- ◆ Chlorine, other disinfectants, used to kill bacteria and other microorganisms in drinking water
- ◆ 1974—USEPA and others discover THMs in drinking water
- ◆ Formed from reaction of chlorine with natural organic matter (NOM)



**Regulatory Framework/Relevant
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Regulatory Framework/Relevant Concerns, *continued*

◆ 1975—USEPA Survey of 80 water systems

- All systems using free chlorine had THMs in final water
- THMs are carcinogenic
- Four THMs:
 - Chloroform
 - Bromodichloromethane
 - Dibromochloromethane
 - Bromoform



Regulatory Framework/Relevant Concerns, *continued*

- **Other DBPs from other disinfectants found since 1970s**
- **Much more work on characterization of organics in water**
 - ◆ **Total organic carbon (TOC) no longer fully adequate**
 - ◆ **No generally accepted standardized approach**



Regulatory Framework/Relevant Concerns, *continued*

- ◆ Humic fraction
- ◆ Fulvic fraction
- ◆ Polar
- ◆ Nonpolar
- ◆ Various isolation methods
- ◆ USGS is a leader in NOM characterization
- ◆ DBP formation potential



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Regulatory Framework/Relevant Concerns, *continued*

- **Basic reaction**
 - ◆ Disinfectant or oxidant and precursors (NOM, bromide) → DBPs
- **DBPs of current interest**
 - ◆ Inorganic DBPs
 - ◆ THMs
 - ◆ Haloacetic acids (HAAAs)
 - ◆ Cyanogen halides



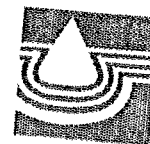
Regulatory Framework/Relevant Concerns, *continued*

- ◆ Halooxacetone nitriles
- ◆ Halooxaldehydes
- ◆ Halophenols
- ◆ Chloralhydrate
- ◆ 3-chloro-4-(chloromethyl)-5-hydroxy-2(5H)-furanone (MEX)



Regulatory Framework/Relevant Concerns, *continued*

- 1979—First DBP regulation
 - ◆ 0.10 mg/L THM
 - ◆ Chloroform appeared to be carcinogenic
 - ◆ Policy assumptions. No safe level exists for human exposure to carcinogens; concentrations of these compounds should be reduced to the extent feasible



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**Regulatory Framework/Relevant
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Regulatory Framework/Relevant Concerns, *continued*

- 1994—Proposed new DBP MCLs
 - ◆ Should be finalized in November 1998; Stage 1 D/DBP Rule
 - 0.080 mg/L for THMs
 - 0.060 mg/L for HAA5
 - 0.010 mg/L for bromate
 - 1.0 mg/L for chlorite
- Basic concern of USEPA and community: No backsliding on disinfection



Regulatory Framework/Relevant Concerns, *continued*

- **How are DBPs relevant to perchlorate?**
- **Best treatment method of perchlorate appears to be biological**
- **Developed systems need carbon source**



Regulatory Framework Relevant Concerns, *continued*

■ Water utility concerns

- ◆ Carry through of microbiological organisms
- ◆ Increase in DBP formation potential
- ◆ Increase in NOM/TOC in finished water and biological regrowth activity in distribution system
- ◆ Changed water quality—inorganic reactions in distribution system
- ◆ Taste and odor concerns
- ◆ Increased disinfectant demand



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Planned 1998 Activities and Schedule

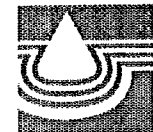
■ Perchlorate-related projects moving forward

- ◆ **Application of Bioreactor Systems to Low
Concentration Perchlorate Contaminated Water**
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by Reverse Osmosis and Nanofiltration**
- ◆ **Treatability of Perchlorate Using Ion Exchange
Technology**
- ◆ **Removal of Perchlorate and Bromate in
Conventional Ozone/CAC Systems**
- ◆ **Investigation of Methods for Perchlorate
Destruction in Aqueous Waste Streams**



Planned 1998 Activities and Schedule

- **Two analytically-related projects
advertised**
 - ◆ **Survey the Performance of the
California DHS (on Chromatography)
Analytical Protocol**
 - ◆ **Short Term Perchlorate Laboratory
Issues**
- **No proposals received**



Planned 1998 Activities and Schedule, continued

- Treatment projects have phased scope
- Intent for realistic/applied projects
- Known conditions
- Phase I: Laboratory/bench scale
- Phase II: Pilot scale
- General Phase I work in proposals
- Pilot-scale specifics identified, and Phase I
- Phase II on Crafton Redlands Plume—
Terms of Congressional earmark



Planned 1998 Activities and Schedule

- Five treatment-related projects moving forward
 - ◆ Application of Bioreactor Systems to Low-Concentration Perchlorate Contaminated Water
 - ◆ Treatability of Perchlorate-Containing Waters by Reverse Osmosis and Nanofiltration
 - ◆ Treatability of Perchlorate Using Ion Exchange Technology
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Planned 1998 Activities and Schedule, continued

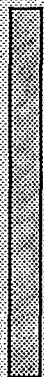

- **Winning proposal by mid-June**
- **Contracts completed 4 to 8 weeks after mid-June**
- **Probably August/September before work**
- **Timetable contingent on USEPA grant released to ENVWID**
- **Many responding teams include both universities and consulting firms**



***Planned 1998 Activities
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MtBE and Perchlorate: Regulatory and Policy Considerations Under the Safe Drinking Water Act

220

MIKE OSINSKI

Office of Ground Water and Drinking Water

U.S. Environmental Protection Agency

Washington, D.C.



Contaminant Identification and Selection Under the SDWA

■ Contaminant Selection Under the 1986 Amendments to the SDWA:

- ⇒ Regulate 83 contaminants by 1989;
- ⇒ Regulate 25 contaminants every 3 years.

■ Congress, EPA had Implementation Concerns:

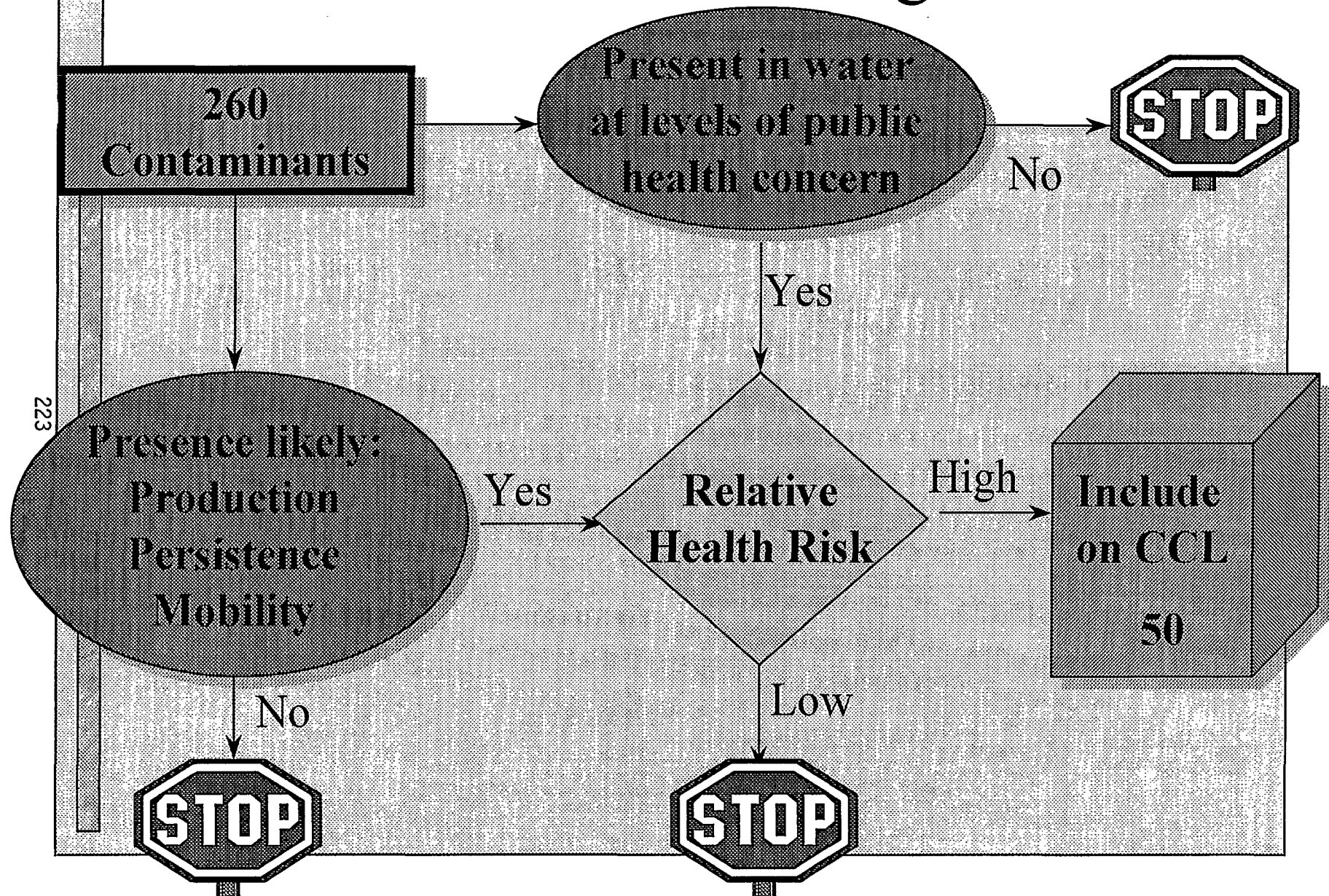
- ⇒ Missed statutory deadlines;
- ⇒ Water systems encountered difficulty in timely compliance, financial capacity;
- ⇒ Focus on sound science and contaminants posing greatest risk.

Contaminant Identification and Selection Under the SDWA

■ Contaminant Selection Under the 1996 Amendments to SDWA.

- ⇒ Publish a Contaminant Candidate List (CCL) of contaminants known or anticipated to occur in DW and not subject to NPDWRs by Feb 1998.
- ⇒ Broad consultation with stakeholders, NDWAC, and SAB.

CCL Chemical Screening Criteria



Contaminant Identification and Selection under the SDWA

■ Draft CCL Published on Oct 6, 1997.

- ⇒ MtBE included.
- ⇒ Did not include perchlorate: sought comment.
- ⇒ Public comments indicated overall support for maintaining MtBE and adding perchlorate.

■ Final CCL published on March 2, 1998.

- ⇒ Contains 50 chemical and 10 microbiological contaminants.

Contaminant Candidate List (CCL)

■ Functions of the CCL:

- ⇒ Make determinations for at least 5 contaminants of whether or not to regulate with a NPDWR by 2001.
- ⇒ Focus and prioritize research agenda for contaminants with data gaps.
- ⇒ Source for selection of contaminants for unregulated contaminant monitoring regulation (UCMR) due in 1999.

MtBE, Perchlorate and the CCL

■ Two categories of contaminants on the CCL:

- ⇒ (1) Regulatory Determination Priorities;
- ⇒ (2) Research Priorities.

■ MtBE and Perchlorate placed in the research priorities category due to extensive data gaps.

- ⇒ MTBE: occurrence; health effects; treatment.
- ⇒ Perchlorate: occurrence; health effects, treatment; analytical.

Where do we get the data for MtBE?

Occurrence	Health Effects	Treatment
CA unreg. monitoring	Human Study: Pharmacokinetics (EPA)	15 – 20 projects underway (academic, gov't, industry)
USGS / EPA 12 State study	PBPK Modeling Studies (EPA, OFA)	Lessons learned from UST remediations
USGS NAWQA program; non-point modeling.	Oral Subchronic / Cancer Mechanistic Studies (OFA, CIIT)	
MWD surface water sampling	2 year Rodent Bioassay (OFA)	
Maine monitoring program	Taste and Odor Studies (OFA)	

Where do we get the data for Perchlorate?

Occurrence	Health Effects	Analytical Methods	Treatment Technologies
CA Monitoring	8 Toxicology Studies (DoD, Industry):	CA DHS	Superfund Pilots
CA MWD		Analytical Industry	Air Force
AWWSC (400 wells, 16 states)	Neurotoxicity Developmental Reproductive	IPSC Collaborative	Academic, Industry Research
Utah monitoring program (summer 98)	Subchronic 90 day Immunotoxicity Genotoxicity		EVWD, AWWARF earmarked appropriation
Superfund, other waste sites	Pharmacokinetics Cancer Mechanistic		
AWWARF vulnerability assessment			

Regulatory and Policy Agenda for MtBE and Perchlorate

- **Determination to regulate not likely by 2001.**
- **MtBE will be included in the proposed UCMR (Fall 1998).**
- **Perchlorate not currently planned for inclusion in the proposed UCMR.**
 - ⇒ Lack of EPA approved analytical method(s).
 - ⇒ Recommend near-term special occurrence studies.

Next Steps for MtBE and Perchlorate

■ MtBE Right Now:

⇒ Provisional Drinking Water Advisory Issued (Dec. 1997).

■ Perchlorate Near Term (1-2 years):

⇒ If health effects and occurrence data warrant, develop a Health Advisory.

■ Longer Term (3 to 5 years):

⇒ Data gaps filled and MtBE and perchlorate moves to the regulatory determination priority category of next CCL -- due in 2003.

EPA Health Advisory Program

■ SDWA General Authority:

⇒ “The Administrator may publish health advisories (HA), which are not regulations, or take other appropriate actions for contaminants not subject to any national primary drinking water regulation.”

■ HAs represent concentrations of contaminant in drinking water which adverse health effects are not expected to occur.

EPA Health Advisory Program

- **Not federally enforceable.**
- **Subject to change as new information becomes available.**
- **Can serve as technical guidance to assist State, Tribal, and local officials responsible for protection of public health.**

MtBE Drinking Water Advisory

■ Consumer Acceptability Advisory.

⇒ Judgement call based on existing organoleptic studies: 20 to 40 ug/L guidance range to avoid unpleasant taste and odor effects.

■ Cancer and Non-Cancer Risk Characterized by Margin of Exposure (MOE).

⇒ Managing to levels of 20 to 40 ug/L provides MOE cancer protection consistent with NPDWRs and 10 to 100 times > provided by RfD for non-cancer effects.

Summary

- MtBE and perchlorate receive the most individual attention w/o specific statutory requirements.
- MtBE and Perchlorate are research and occurrence priorities for the OGWDW.
 - ⇒ Developing short and longer term research plans on health, treatment, and analytical methods.
- EPA is very engaged in the IPSC.

How would EPA use a RfD in developing a Health Advisory?

- **Determine RfD in mg/kg/day.**
- **Determine DWEL (Drinking Water Equivalent Level) in mg/L, assuming 100% drinking water contribution.**
- **Determine HA in mg/L.**

Sample HA Calculations

■
$$\text{DWEL (mg/L)} = \frac{(\text{RfD})(70 \text{ kg adult})}{(2 \text{ L/day})}^*$$

$$\text{DWEL (mg/L)} = \frac{(\text{RfD})(10 \text{ kg child})}{(1 \text{ L/day})}^{**}$$

* *for lifetime HA*

** *for 1 day, 10 day, and longer term HA*

■
$$\text{HA (mg/L)} = (\text{DWEL})(\% \text{ DW contribution})$$

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APPENDIX
Visuals For Previously Published Papers

Mechanism and Efficiency of the Degradation of MTBE in Contaminated Groundwater and Potable Water by the UV/H₂O₂ Process

James R. Bolton*, Ali Safarazadeh-Amiri*,
Stephen R. Cater, Bertrand Dussert,
Mihaela I. Stefan* and John Mack*

*Calgon Carbon Corporation
*The University of Western Ontario



Outline

- ▶ Introduction - the MTBE problem
- ▶ Regulations
- ▶ Treatment options
- ▶ The UV/H₂O₂ Process
- ▶ The EE/O Figure of Merit
- ▶ Treatment results
- ▶ Intermediates
- ▶ Mechanism
- ▶ A case study
- ▶ Conclusions

The MTBE Problem

- ▶ Ethanol and mostly MTBE are the primary oxygenates used to meet the oxygen content requirement of reformulated gasoline.
 - ▶ MTBE is highly water soluble and leaks from underground storage tanks and pipelines have contaminated groundwater supplies for potable water.
-
-

MTBE Regulations

- ▶ Not currently regulated as a drinking water contaminant
 - ▶ MTBE is now on the USEPA Drinking Contaminant Candidate List
 - ▶ USEPA has tentatively classified MTBE as a possible human carcinogen
 - ▶ MTBE has a low taste and odor threshold (15-40 ppb).
 - ▶ USEPA recently issued a drinking water advisory limit of 20-40 ppb.
-

Treatment Options

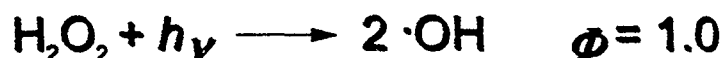
- ▶ Air stripping - requires high air-to-water ratios - must treat off-gas
 - ▶ Activated carbon adsorption - carbon has a low affinity for MTBE
 - ▶ Biological treatment - not suitable for very low concentrations
 - ▶ Advanced Oxidation Technologies -
UV/H₂O₂, UV/O₃, O₃/H₂O₂ processes
-
-

Advanced Oxidation Technologies (AOTs)

- ▶ Based on the generation of highly reactive hydroxyl radicals.
- ▶ UV/O₃ and O₃/H₂O₂ work, but if water contains bromide, bromate will be formed. It also generates an off gas.
- ▶ UV/H₂O₂ involves UV photolysis of H₂O₂ to generate hydroxyl radicals - bromate is not formed.

The Rayox UV/H₂O₂ Process

- ▶ Hydrogen peroxide absorbs UV in the 200-300 nm range.



- ▶ Must have a UV lamp with a strong output in the 200-300 nm range.
 - ▶ The hydroxyl radicals attack and oxidize most organic pollutants with very high rate constants.
-
-

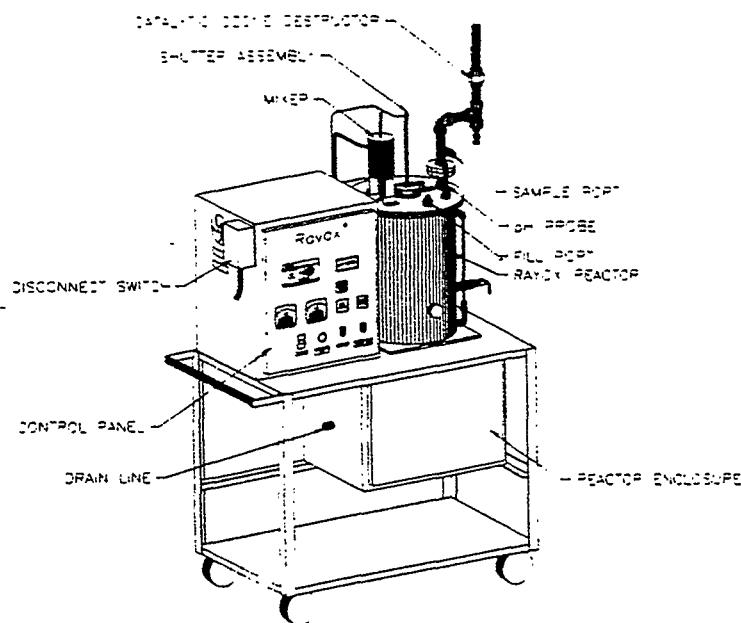
Figure-of-Merit for AOTs

- ▶ Most AOTs treatments follow first-order kinetics.
- ▶ *Electrical Energy per Order (EE/O)* as the electrical energy (kWh) necessary to reduce the concentration of a pollutant by one order of magnitude in 1000 US gallons (3785 L) of water

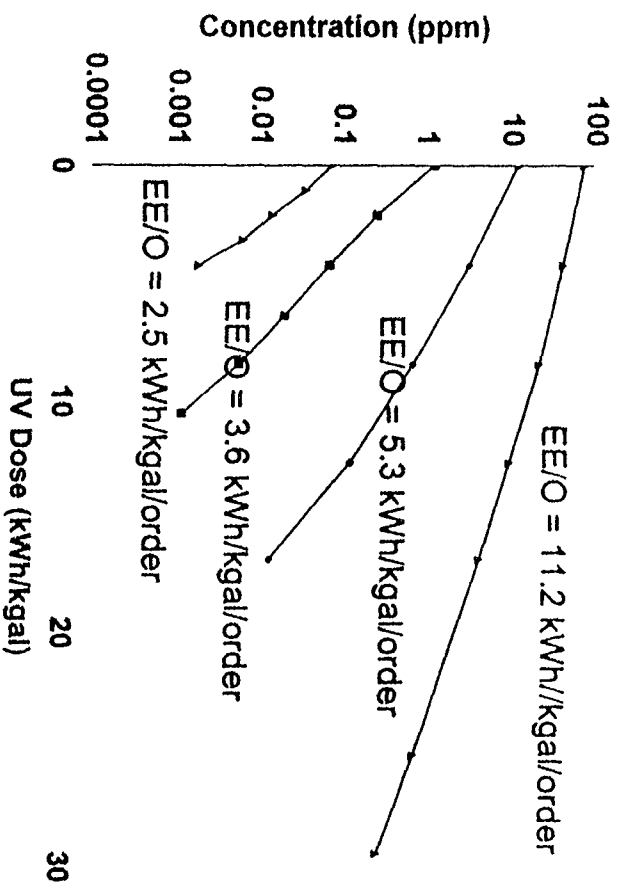
Experimental

- ▶ UV/H₂O₂ treatments carried out in a 1 kW Rayox UV true batch reactor.
- ▶ H₂O₂, MTBE and other contaminants (e.g., BTX) were spiked into Toronto tap water. A "t = 0" sample taken.
- ▶ UV lamp turned on (under a shutter) allowed to warm up; shutter raised at t = 0.
- ▶ Samples taken at increasing UV doses for analysis.

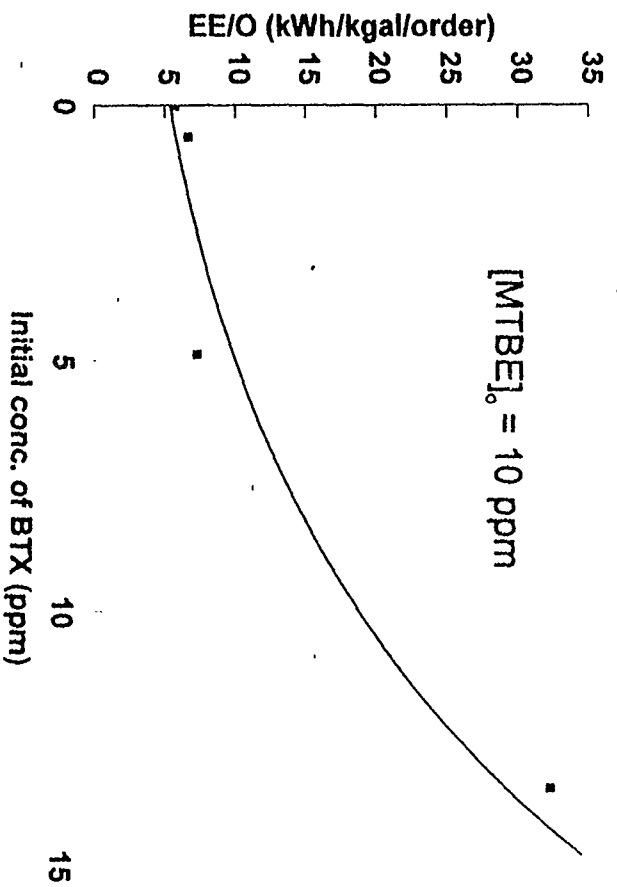
Batch 1 kW UV Reactor



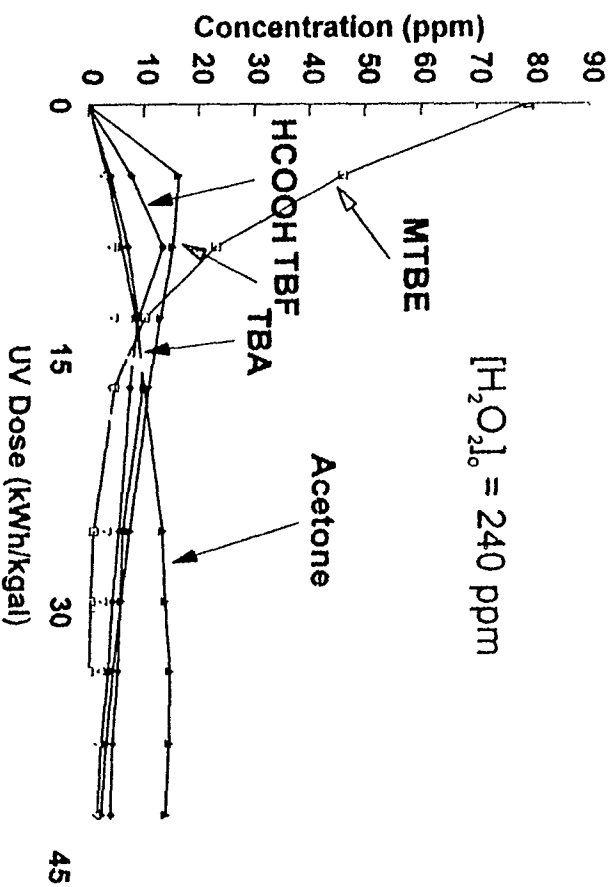
Dependence of EE/O on [MTBE].



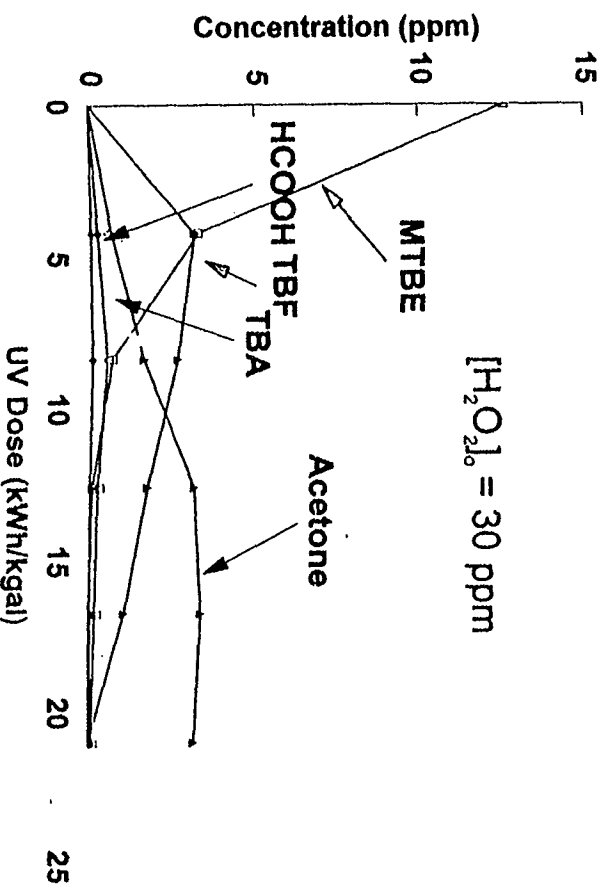
Dependence of EE/O on [BTX].



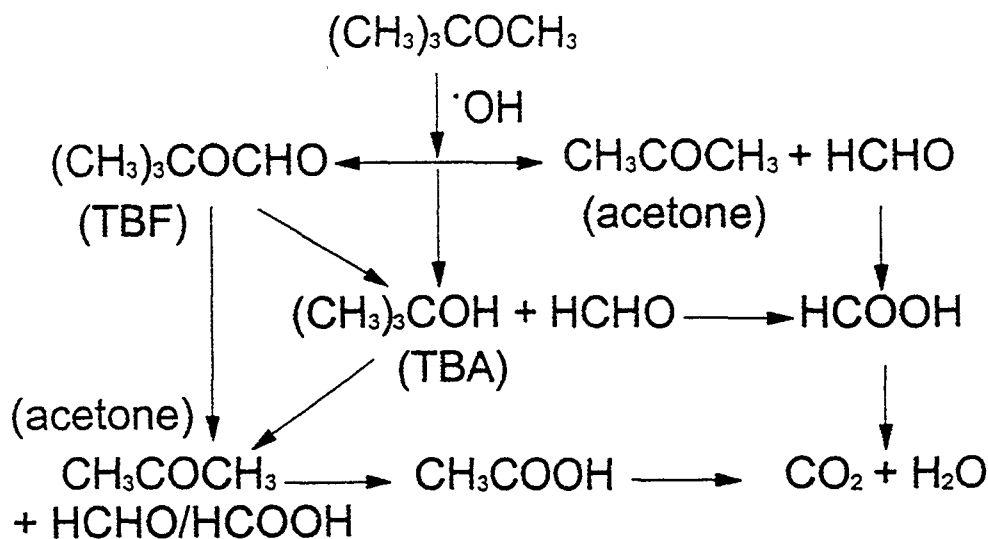
UV/H₂O₂ Treatment of MTBE



UV/H₂O₂ Treatment of MTBE



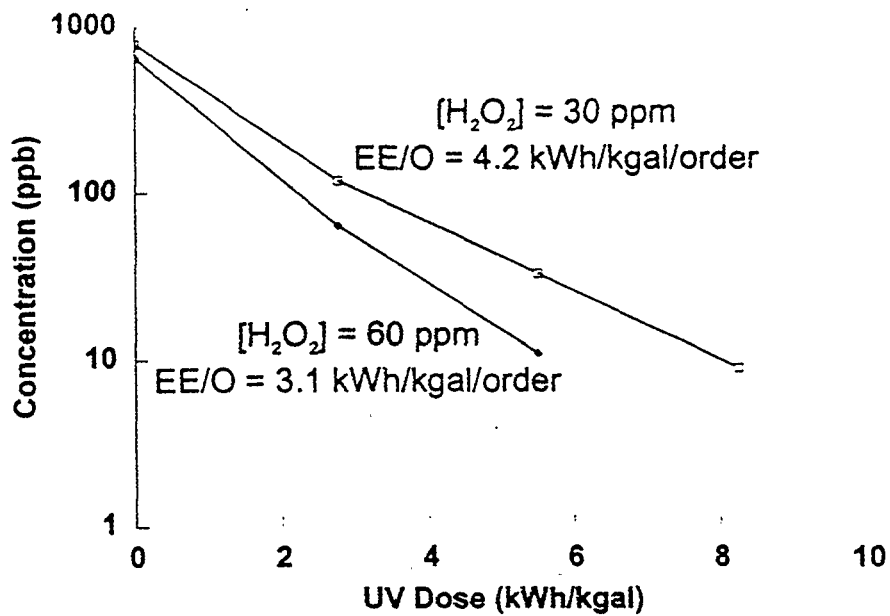
Simplified Mechanism



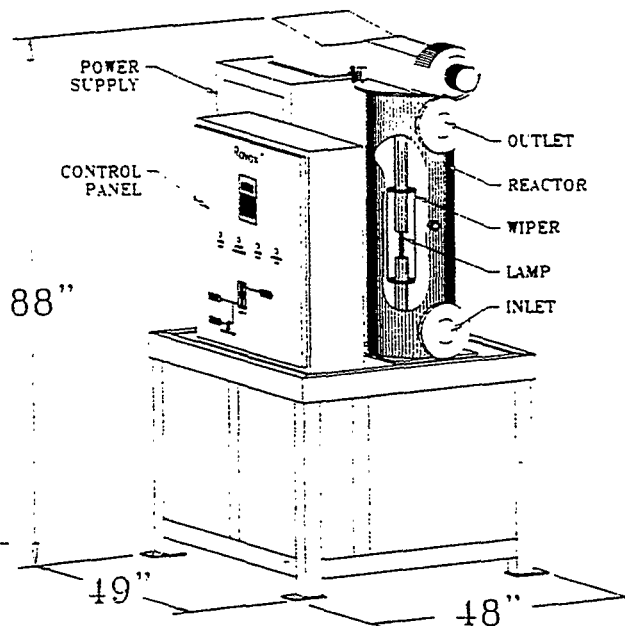
A Case Study

- ▶ Tests were carried out on an MTBE contaminated drinking water.
- ▶ As received the water had <50 ppb MTBE.
- ▶ The water was spiked with MTBE (700 ppb), TCE (20 ppb) and PCE (20 ppb) to simulate the worst case scenario.
- ▶ Two runs were carried out at 30 and 60 ppm H_2O_2 .

Test Results



Rayox UV/H₂O₂ Reactor



Cost estimates

- For a water flow rate of 1000 gpm, a 14 x 23 kW UV lamp system in a Rayox tower (60 ppm H_2O_2) would reduce the concentration of MTBE from 700 to 5 ppb (in the tower, EE/O = 2.5 kWh/kgal/order).
- The capital cost would be \$395,000 and an operating cost of \$0.61 per 1000 gal.

Treatment Costs vs. [MTBE]

[MTBE] (ppm)	EE/O (kWh/kgal/order)	Operating Cost* (\$/kgal)
0.1	2.0	\$0.28
1.0	2.5	\$0.57
10	5.0	\$1.55
100	18	\$7.52

* Cost to achieve an effluent level of 10 ppb.

Conclusions

- ▶ The UV/H₂O₂ process is effective and economic.
 - ▶ Intermediates have been detected and a simplified mechanism proposed.
 - ▶ The intermediates are at a low level and are non-toxic.
 - ▶ Presence of BTX has little effect on EE/O for BTX levels < 5 ppm.
 - ▶ Intermediates are non-toxic and treat readily with further UV dose.
 - ▶ No bromate is generated from bromide.
-

Application of the RBCA Framework for MTBE

Curtis Stanley, George DeVaul, and John Gustafson



Presented at the

NGWA - Southwest Focused Ground Water Conference

(MTBE and Perchlorate Issues)

June 3, 1998

Anaheim, CA

Risk-Based Corrective Action (RBCA) Process

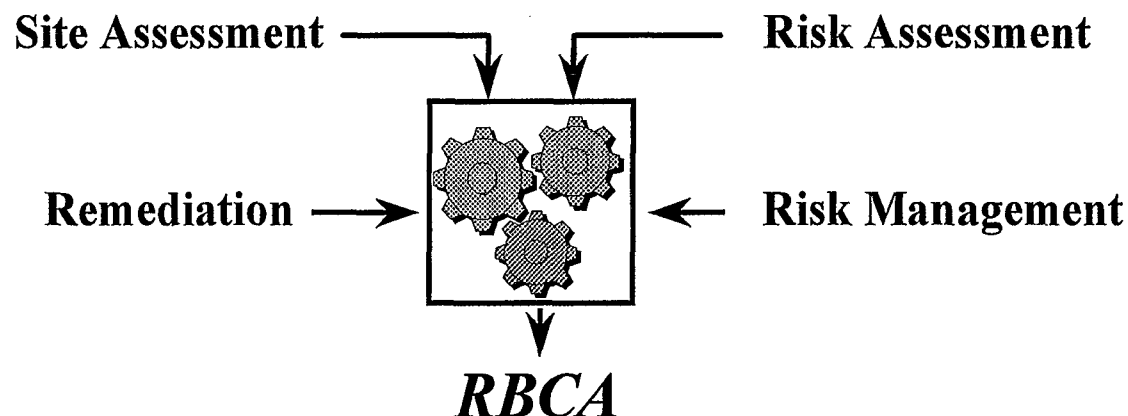
RBCA is a **framework** developed by ASTM in which exposure and risk assessment practices are integrated with traditional components of the corrective action process.

RBCA Goals:

- ☒ protection of human health and environment
- ☒ consistent and technically-defensible
- ☒ appropriate and resource-efficient remedies are selected
- ☒ optimal allocation of limited resources
- ☒ practical and resource-efficient approach
- ☒ allow corrective action and redevelopment to proceed together

How does RBCA Work ?

RBCA is a 3-tiered framework that allows the user to make cost-effective risk management decisions. It integrates the following:



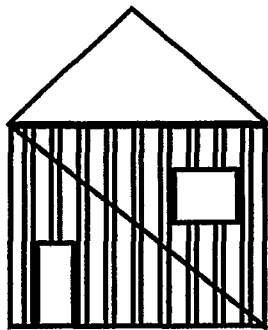
Result: RBCA framework, or philosophy, upon which regulatory agencies can build their own customized risk-based guidance.

How is a RBCA Program Developed and Implemented?

ASTM Risk-Based Corrective Action - outlines a framework for integrating exposure and risk assessment practices with traditional components of the corrective action process.

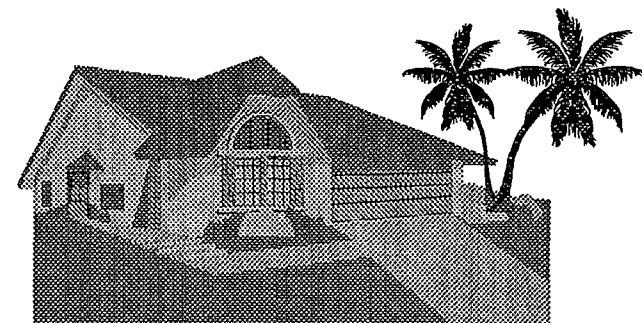
- Describes steps and philosophy to build the framework and to incorporate risk management decisions into corrective action programs.
- Sensitive to regulatory agency policies.
- Provides appendices which serve as examples only for program consideration.

*** It is the difficult responsibility of the implementing organization to understand the technical and policy issues and to develop them in a way which enhances the state and/or regulatory program.**



RBCA Framework

Policy Decisions →



Regulatory Program

Stakeholder Group Utilization

- Stakeholders are anyone who can influence or be affected by the outcome of the process.
- Use of a stakeholder group to develop RBCA programs helps ensure that issues are well understood and dealt with in a reasonable manner.
- Stakeholder groups can be effective in bringing about regulatory and/or legislative change, when needed.

Initial Program Development

Objective - To provide a strong technical base rather than an emotional base for making risk-based decisions.

- Understanding of the RBCA Process
- Understanding of technical issues
 - Fate and Transport
 - Risk Assessment
- Understanding of policy issues

TRAINING

Intermediate Program Development

(Resolving the Tough Issues)

Developing Technical/Policy Guidance

- Risk Assessment Requirements
- Fate and Transport Requirements
- Tiered Data Requirements
- Institutional Issue Guidance
- Risk Management Guidance

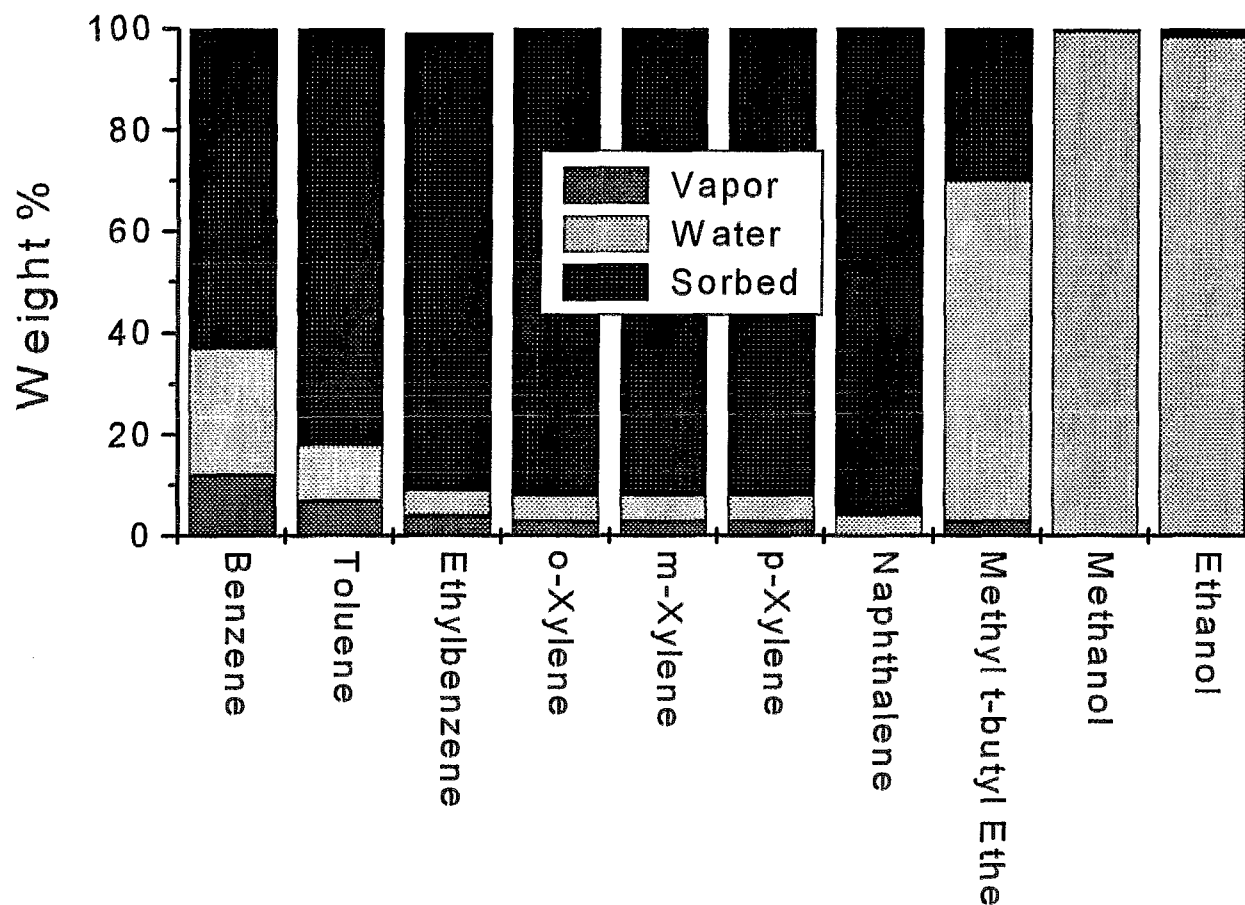
Physical/Chemical Properties

Compound	MW	S (mg/l)	ρ (g/ml)	Pvap (atm)	H (c/c)	Koc	R
Benzene	78	1780	0.88	1E-01	0.22	81	4
Toluene	92	515	0.87	4E-02	0.27	234	11
Ethylbenzene	106	152	0.87	1E-02	0.36	537	25
o-Xylene	106	220	0.88	1E-02	0.23	557	26
m-Xylene	106	160	0.87	1E-02	0.29	612	28
p-Xylene	106	215	0.86	1E-02	0.23	590	27
Naphthalene	128	31	1.15	4E-04	0.02	844	39
Methyl t-butyl Ether	88	42000	0.74	3E-01	0.02	14	1.6
Methanol	32	miscible	0.79	1E-01	0.0001	0.2	1.0
n-Ethanol	46	miscible	0.79	5E-02	0.0012	0.5	1.0

Ref: after TPHCWG Volume #3 (draft)

$R = \text{retardation} = 1 + \rho_b * f_{oc} * K_{oc} / \eta$ w/ ASTM RBCA Default Parameter Values

Phase Distribution



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Effective Solubility

Compound	Mole %		Effective Solubility (mg/L)	
	Min	Max	Min	Max
Benzene	0.1	3.5	2	62
Toluene	2.7	21.8	14	112
Ethylbenzene	0.4	2.9	1	4
o-Xylene	0.7	2.9	1	6
m-Xylene	1.8	3.9	3	6
p-Xylene	0.8	1.6	2	3
Naphthalene	0.02	0.02	0.006	0.006
Methyl t-butyl Ether	0.0	15.0	0	6300

**High solubility and mole percent of
MTBE in gasoline results in potential
MTBE source concentrations > BTEX!**

Orange County MTBE Data Extrapolation

Percentile Conc. (ppb)

10	4
20	20
30	70
40	210
50	490
60	1400
70	3400
80	10500
90	41000
100	900000

95th Percentile Conc. = 75,000 ppb

Average Conc. = 95,709 ppb

Median Conc. = 945 ppb

(332 sites)

Concentration Reduction Factor (CRF)

The concentration reduction factor (CRF) is the ratio between a chemical's source area solubility and the concentration of that chemical which is protective of a receptor. The CRF provides a means to help assess fate & transport models for evaluating plume attenuation lengths. Additionally, it can be used to evaluate remedial options.

$$CRF = C_{\text{source}} / C_{\text{receptor}}$$

Benzene

Concentration Reduction Factors (CRF)

- **Benzene**

- $C_{\text{source (max)}} = S \cdot MF = (1750 \text{ mg/L} \cdot 0.02) = 35 \text{ mg/L}$
- $C_{\text{source(95\%)}} = 10 \text{ mg/L}$ (personal experience)
- $C_{\text{receptor}} = 0.005 \text{ mg/L}$
- $C_{\text{source}} / C_{\text{receptor}}$ (CRF **max**) = **7000**
- $C_{\text{source(95\%)}} / C_{\text{receptor}}$ (CRF 95%) = **2000**

MTBE

Concentration Reduction Factors (CRF)

- **MTBE**

- $C_{\text{source (max)}} = S \cdot MF = (42\,000 \text{ mg/L} \cdot 0.15) = 6300 \text{ mg/L}$
- $C_{\text{source(95\%)}} = 75 \text{ mg/L}$ (Based on Orange County data for 332 sites)
- $C_{\text{receptor}} = 0.02 \text{ mg/L}$
- $C_{\text{source}} / C_{\text{receptor}} \text{ (CRF max)} = \mathbf{315\,000}$
- $C_{\text{source(95\%)}} / C_{\text{receptor}} \text{ (CRF 95\%)} = \mathbf{3750}$

Plume Attenuation Length (PAL)

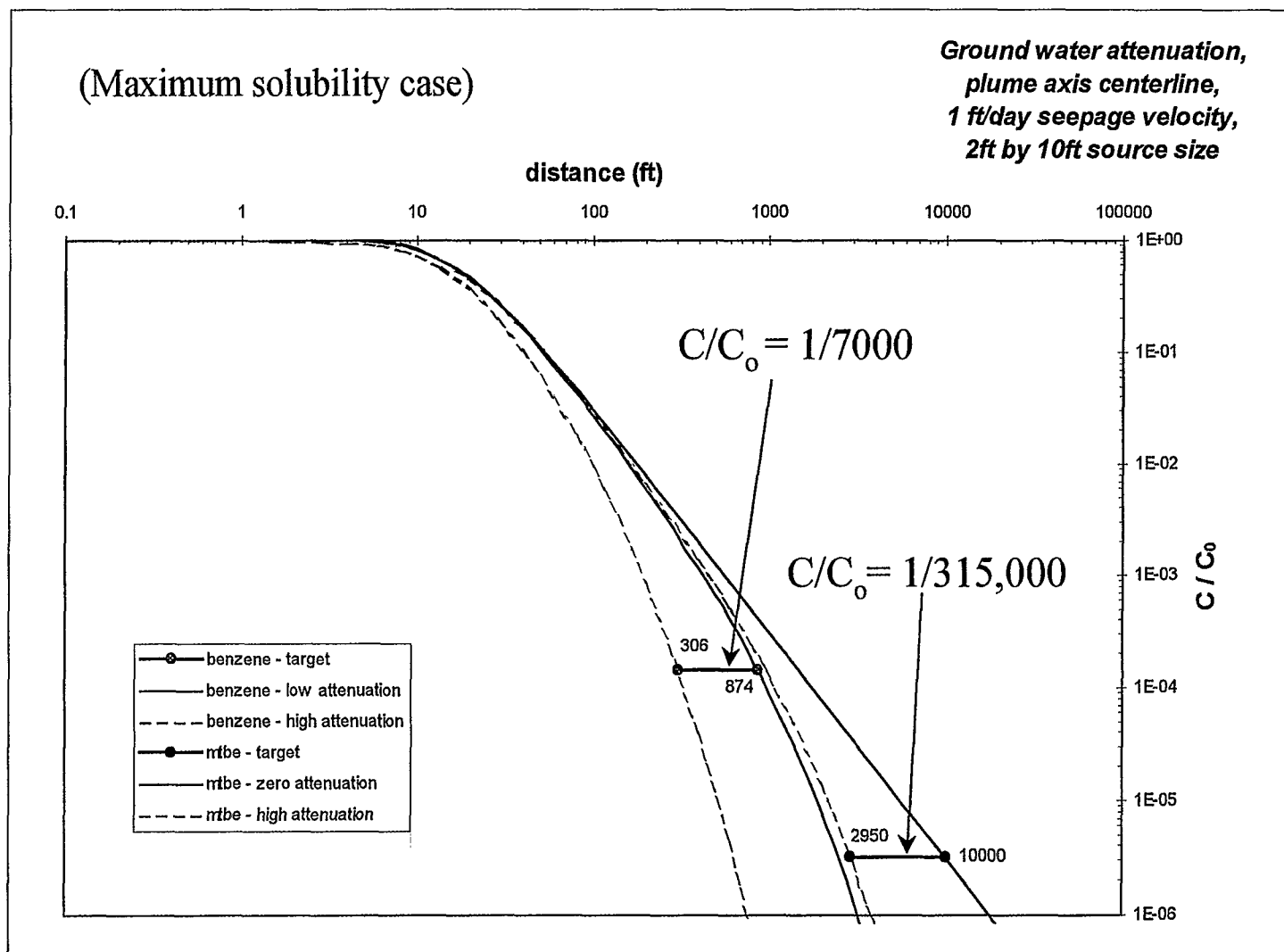
- The plume attenuation length is the distance at which a stabilized plume meets an acceptable concentration that is protective of the receptor.
- A receptor located inside the plume attenuation length has a potential to be exposed to an unacceptable concentration
- A receptor located outside the plume attenuation length, will not be adversely affected.

Groundwater Fate & Transport

Key Assumptions

- Dispersion in groundwater (*all chemicals*)
 - molecular diffusion, flow path variability, sorption-desorption kinetics
- Benzene
 - attenuation: 0.01 to 0.001 /day
 - aerobic microbial degradation (with O₂ present)
- MTBE
 - attenuation: 0.001 to 0 /day
 - aerobic microbial degradation (maybe), volatilization, model variability

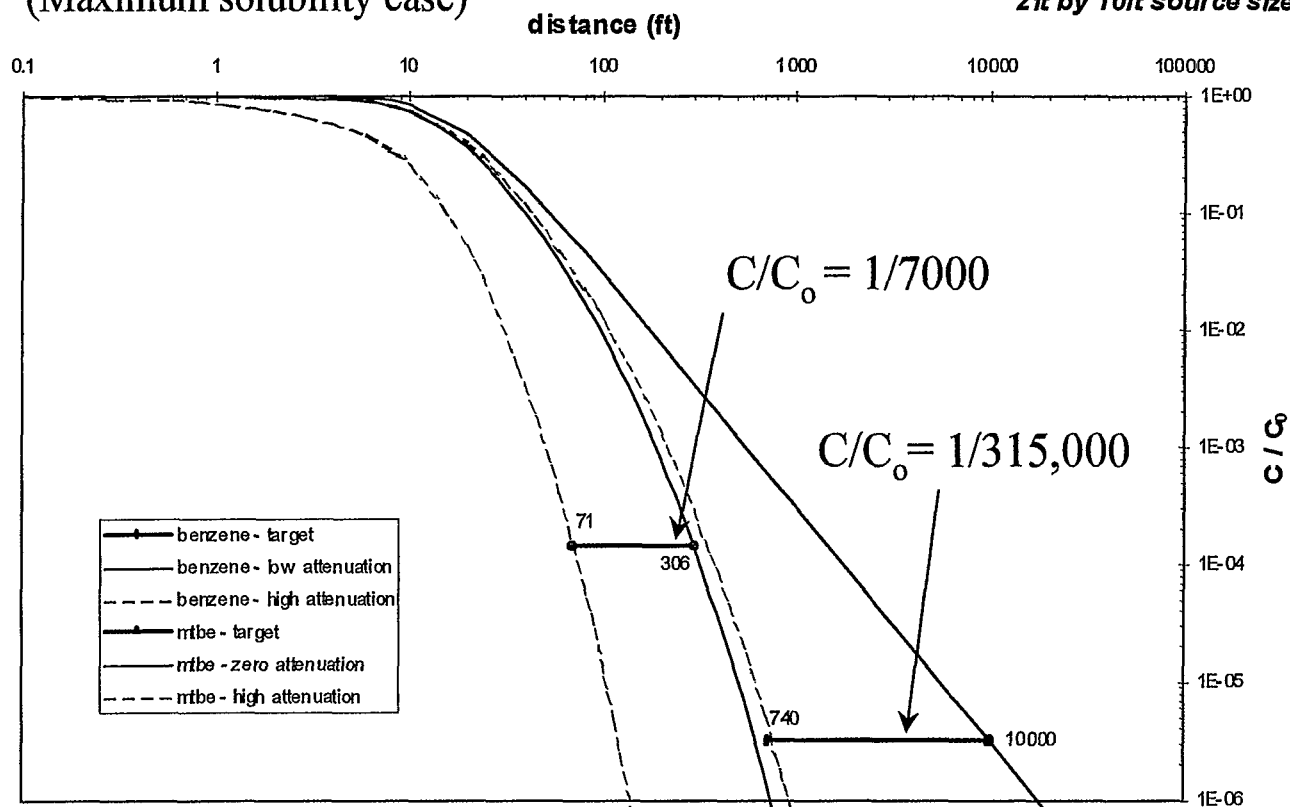
Example: Conservatively Modeled Plume



Example: Modeled Plume

(Maximum solubility case)

Ground water attenuation,
plume axis centerline,
0.1 ft/day seepage velocity,
2 ft by 10 ft source size

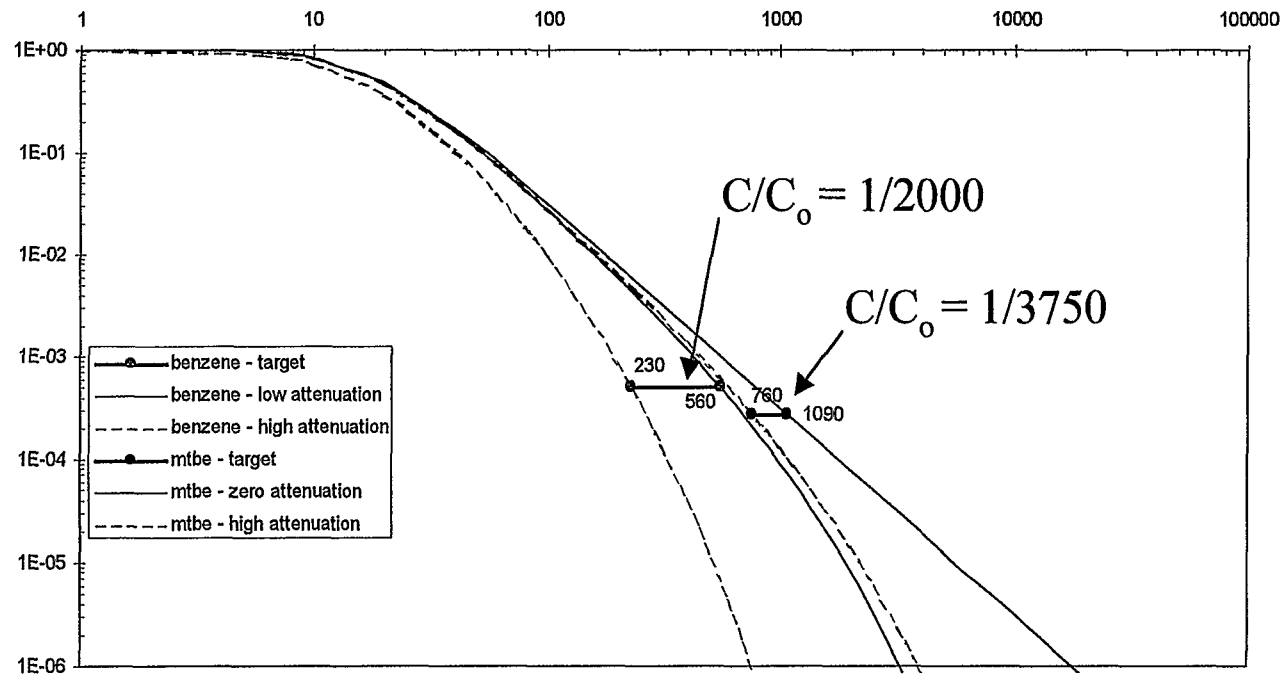


MTBE Fate and Transport

Orange County - 95 Percentile

Maximum MTBE Concentrations

Ground water attenuation,
plume axis centerline,
1.0 ft/day seepage velocity,
2ft by 10ft source size

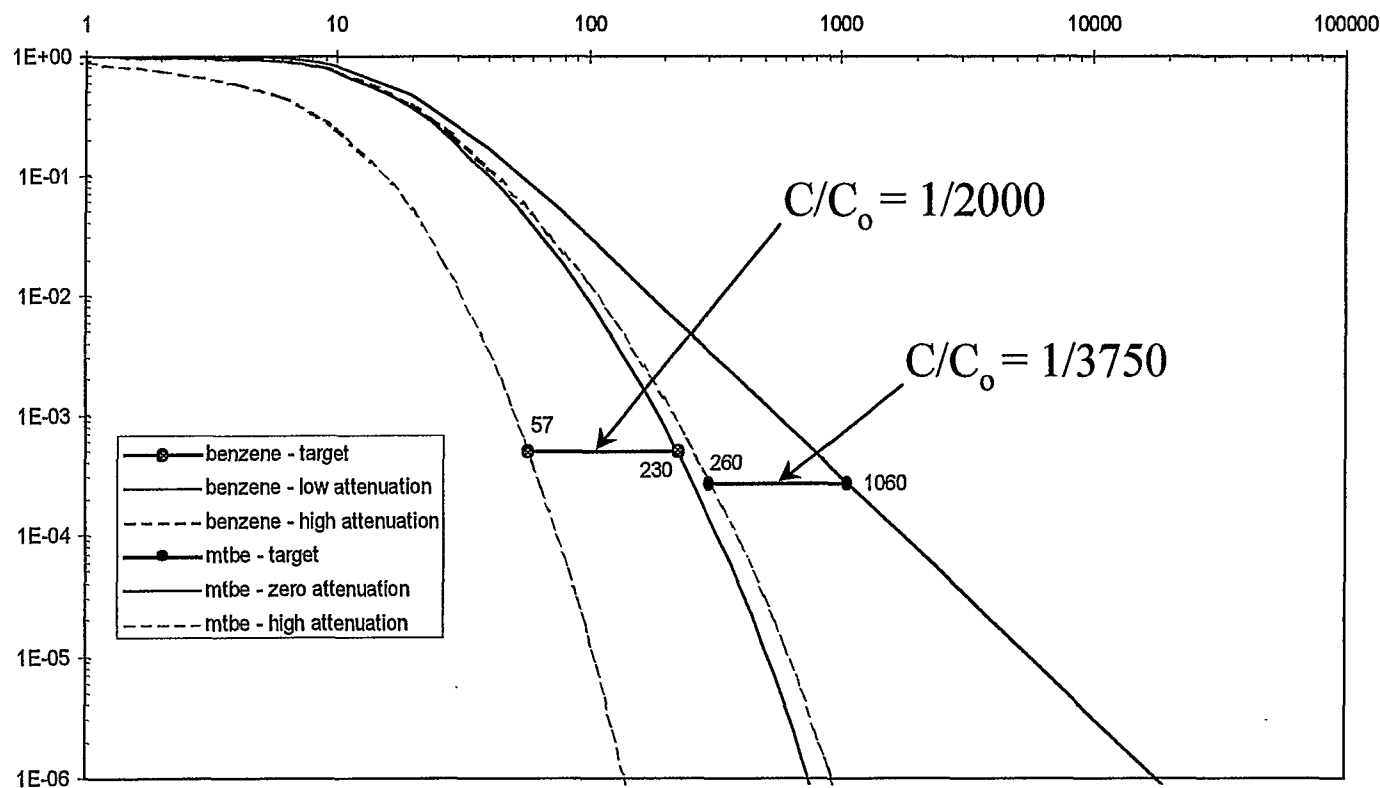


MTBE Fate and Transport

Orange County - 95 Percentile

Maximum MTBE Concentrations

Ground water attenuation,
plume axis centerline,
0.1 ft/day seepage velocity,
2ft by 10ft source size



Comparison of MTBE and Benzene PAL's

- Benzene
 - $V_s = 1$ ft/day
 - PAL_{max} ranges between 306 and 874
 - $PAL_{95\%}$ ranges between 230 and 560
 - $V_s = 0.1$ ft/day
 - PAL_{max} ranges between 71 and 306
 - $PAL_{95\%}$ ranges between 57 and 230
- MTBE
 - $V_s = 1$ ft/day
 - PAL_{max} ranges between 2950 and 10,000
 - $PAL_{95\%}$ ranges between 760 and 1090
 - $V_s = 0.1$ ft/day
 - PAL_{max} ranges between 740 and 10,000
 - $PAL_{95\%}$ ranges between 260 and 1060

RBCA Analysis - Focus on Key Issues for Recalcitrant Compounds

Simple RBCA generic analyses can help identify critical technical and policy issues (shown below) which need resolution. As stakeholders address these issues, the final RBCA program is protective and resource-efficient.

- **Fate & Transport vs Receptor Location**
- **Reasonable Groundwater Classification**
- **Site Categorization**
- **Leak/Spill Prevention** (unacceptable release rates)
- **Model Use and Data Verification**
- **Assessment Criteria**
- **Institutional Controls**

Final Program Development

- Regulatory/Legislative Adjustment
- Tool Development
 - Worksheets, Spreadsheets (Lookup Tables), Simple Models, Guidance Documents.
- Pilot Projects
- Fine Tuning
- Program Implementation
 - **TRAINING**